# TEXTILE RESEARCH JOURNAL

VOLUME XXIV August, 1954 NUMBER 8

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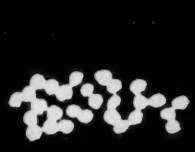

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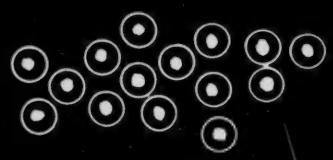

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# TEXTILE RESEARCH JOURNAL

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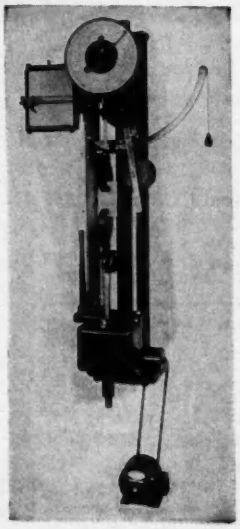

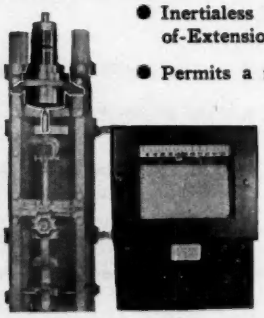

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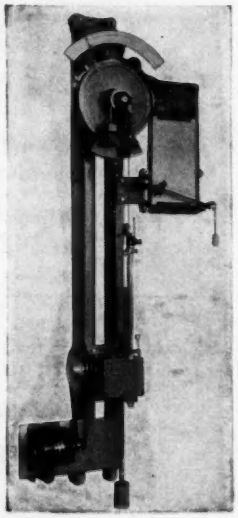

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TEXTILE RESEARCH JOURNAL

VOL. XXIV, No. 8 AUGUST, 1954

# The Swelling of Hair and a Viscose Rayon Monofil in Aqueous Solutions*

**William S. Barnard† and Howard J. White, Jr.‡**

*Textile Research Institute and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey*

**Abstract**

Equipment for measuring the swelling of nearly round single fibers in a variety of solutions is described and has been used to make measurements on the swelling of human hair and a viscose rayon monofil. In particular, measurements have been made on the swelling of both types of fiber in various alkali halide solutions and of the hair in HCl solutions. Except for NaCl solutions, the solutions used in this work caused swelling beyond that caused by liquid water, indicating that the solutes were absorbed by the fibers.

The results using LiCl and LiBr solutions are noteworthy in that considerably more swelling occurs in these solutions than in water. The increase in swelling over the water-swollen value is about 25% in the case of hair and 60% in the case of rayon. The high degrees of swelling of hair must be reached by successive replacement with increasingly concentrated solutions, direct immersion of a water-swollen hair into a concentrated solution causing deswelling. For the viscose rayon, either method causes similar swelling.

The swelling changes in hair caused by altering the different variables common in an acid dye bath for wool have also been studied.

## Introduction

When a hydrophilic fiber which has been brought to equilibrium with liquid water is immersed in an aqueous solution, the normal swelling which results from the immersion of the fiber in water is usually changed. The degree of swelling and its change with the concentration of the solution give information on the interaction between the fiber and the solute of the solution. For example, if the fiber is impermeable to the solute, a decrease in swelling is to be expected because of the lowering of the vapor pressure of water by the solute. On the other hand, if the solute itself is absorbed appreciably, this decrease in swelling can be overbalanced by an increase resulting from the absorbed solute with an over-all increase in swelling as the net result. Osmotic absorption of water is also possible if ions are absorbed by the fiber. Finally, if the water within the fiber fills a system of micropores and the solute is not specifically absorbed by the fiber, the solution will fill the micropores without change in volume of the fiber.

Some results on the swelling of human hair and of a viscose rayon monofil are given in this paper. Direct microscopic measurements of the swelling were made. Since the work was undertaken as part of a program on dyeing, most of the experiments were related to various aspects of dyeing procedures.

In the acid dyeing of keratin fibers, of which human hair is an example, there are four factors which can influence the swelling—namely, the pH, the dye, the added salt, and the temperature. Results are

*Taken in part from a thesis submitted by William S. Barnard in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

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given on the effect of pH and temperature separately on the swelling of hair and on the swelling in one representative dye bath. Swelling in several alkali halide solutions has also been studied.

The swelling of the viscose monofil has been studied less extensively. Results are shown for several alkali halide solutions.

## Experimental

The swelling measurements were made microscopically in a small cell designed to operate at temperatures up to 90°C, and to be inert to strong acids up to about 1*N* and to concentrated salt solutions.

### *Apparatus*

The microscope cell is shown in Figure 1. The main body of the cell is made of a cotton-impregnated phenol formaldehyde resin called "Textolite." The jig and the inlet and outlet nipples are made of 303 stainless steel. All other metal parts which do not come in contact with the immersion liquids are brass, except for a phosphor-bronze spring provided to keep the fiber under a slight tension. The windows of the cell are 24 × 50 mm. cover slides and are cemented in with a phenolic resin varnish, Bakelite type (BJ-16320), a viscous partially polymerized resin which sets on exposure to air to make a waterproof seal. The cement is soluble in alcohol and ether so that the cell should not be used, in general, with organic liquids.

The cell is used in a vertical position. The jig is made from a cylindrical rod and is conical at the bottom. The point of the jig fits into a conical slot in the cell to ensure reproducible alignment of the jig in the cell. The jig has a small screw clamp just above the conical point to hold the fiber. The spring also has a small screw clamp to hold the upper end

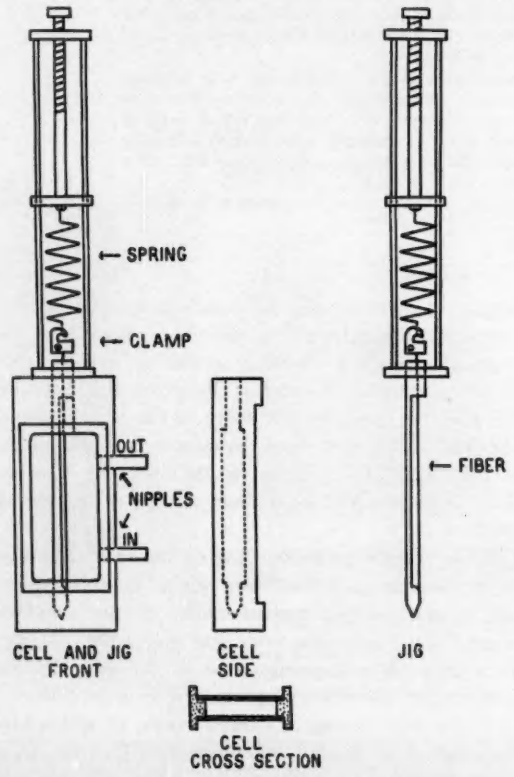


FIG. 1. *Apparatus for measuring fiber swelling microscopically.*

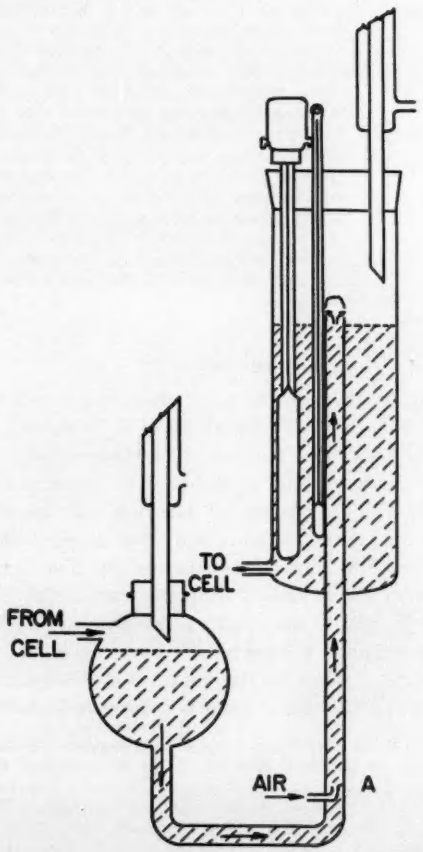


FIG. 2. *Flow system for use with microscope cell.*

of the fiber. Slightly more than three-quarters of the central portion of the jig is cut away, leaving a little less than a quadrant of the rod in the region in which the fiber is mounted. The fiber is mounted as closely as possible to the axis of the jig. Using this arrangement, two profiles of the fiber 90° apart can be made visible in the microscope by turning the jig. Stops (not shown in Figure 1) are provided on the top of the cell to ensure two reproducible settings of the jig, and hence two reproducible profiles of the fiber. If care is taken in making the jig, the fiber can be positioned 1 or 2 mm. from the top cover slide for either profile, and thus a 21 × objective having a working distance of 8 mm. can be used. The other dimensions of the cell and jig are not critical. The rotation of the fiber is necessary because fibers are usually not circular in cross section.

For most of the measurements the cell was simply filled with liquid at room temperature. For cases in which temperature control was desired, the flow system shown in Figure 2 was employed. The flow system is a simplified version of that used in the "dyeometer" [9]. The main reservoir is wound with two 22-ohm Chromel wire coils. One coil is connected across the output of a Variac and set to keep the bath a degree or so below the desired temperature. The other is controlled by the thermoregulator which is immersed in the main reservoir. A temperature control of a few tenths of a degree at 90°C is obtained. Condensers prevent evaporation. Flow through the cell into the overflow reservoir occurs because of gravity. The return flow is provided by the jet of gas introduced at *A*.

*Preparation of Materials*

All samples of hair used were taken from a single head of blonde hair, and only unmedullated hairs were used.* The hairs had an average diameter of 50 $\mu$ and were selected to minimize ellipticity. This was done to increase the accuracy with which the cross-sectional area could be measured using two profiles 90° apart. The diameter was determined at three angles at frequent intervals along the hair. If the ellipticity in percent is defined by

$$200\left(\frac{a-b}{a+b}\right),$$

where $a$ is the largest diameter measured at a position along the fiber and $b$ the smallest, the fiber was accepted only if the ellipticity was uniformly less than 10%.

The hairs were washed in water, extracted with methyl alcohol, ether, and methyl alcohol again. The extractions were of at least one hour's duration. The extracted fibers were then washed with water for several hours at room temperature. No preliminary buffering or special dialyzing was used.

The viscose rayon used in these experiments was an experimental monofil of about 65 $\mu$ average diameter, with an average ellipticity of less than 4%, and essentially without bulges or taper.†

The viscose was extracted and washed by the techniques used with hair, and mounted on the jig.

The salts used were reagent grade except for the LiCl and LiBr. These were obtained in a technical grade. They were purified by solution, treatment with activated carbon, filtration, and finally recrystallization. For all salts, saturated solutions were made and diluted to the appropriate concentration. The exact concentrations of the LiBr solutions were determined by analysis of the halide content by titration with silver nitrate using fluorescein as an indicator. For the other salts, solubility values taken from the literature were used to determine the concentration.

The acid solutions were made up using a pH meter for solutions of pH greater than 1. The concentrations of the solutions of lower pH were determined by titration, with one exception as noted.

*Procedure*

The microscope was used with the barrel horizontal. The cell was fastened to the movable stage of the microscope in such a way that it could be moved up and down. The vertical position of the stage could be determined from a vernier scale which was helpful in reproducing settings. A 21 × objective and filar micrometer eyepiece were used, giving a total magnification of 260 ×.

The fiber was mounted on the jig, and two or three dabs of resin cement were dried to it to serve as reference points. After the jig was fitted into the cell, the cell was filled with water, and 24 hrs. were allowed for equilibrium swelling to be reached. The fiber diameter was read at 15 points about 0.5–1.0

* These samples were obtained through the courtesy of the Friez Instrument Division, Bendix Aviation Corporation, Towson, Md.

† The sample was obtained through the courtesy of Dr. A. C. Walker of Bell Telephone Laboratories, Murray Hill, N. J.

mm. apart. The points were chosen with reference to some distinctive feature of the hair's profile. The vernier setting plus a rough sketch of the relationship of the points to the distinctive surface feature of the hair enabled the same point to be found again for the next set of readings. The process was then repeated at the same intervals for the other profile. In this way, 15 cross sections of the fiber were selected and measured for each set of experimental conditions. Since variations along the fiber are often large compared to changes resulting from changes in the experimental conditions, it was necessary to compare the same cross sections as much as possible to minimize errors resulting from tapering or bulging of the fiber. The relation of the surface features to the permanent reference marks was noted in case one of the features was lost.

Each set of 15 points was measured twice, and the sums of the apparent diameters were taken. The readings were rechecked if the repeat sums varied by more than 0.1% An average diameter was determined for each profile, and the two average diameters were substituted into the formula for the area of an ellipse to determine the average cross-sectional area. The use of any two orthogonal diameters of an ellipse of ellipticity less than 10% introduces an error of less than 0.5% in the area of the ellipse. The statistical standard error of the mean for any one average area was about $\pm 0.5\%$ [1, 15, 21].

Length changes were easier to measure. The length between two of the fiducial marks on the hair was measured. Since the marks could be as much as 10 cm. apart, a considerable degree of precision could be obtained. However, it was found that in all the solutions studied the length changes made a negligible contribution to the total volume change, and they were not recorded. (It should be remembered that the water-swollen state was used as a reference state.)*

All measurements were made at room temperature ($\sim 22°C$) except where noted. The solutions were changed occasionally during treatment of the fibers to ensure that the concentration of the solution was not appreciably altered by the fiber or by remnants of previous solutions. The bath-to-fiber ratio was, of course, very large. A minimum of 24 hrs. was allowed for equilibrium. This was considered to be adequate from preliminary experiments (see discussion of results, however).

## Results and Discussion

### *Swelling of Hair in Alkali Halide Solutions*

The results are reported as percentage increase in volume over the volume of the water-swollen fiber.

* It was pointed out by the reviewer that supercontraction of hair might be expected in some solutions, for example, in concentrated LiBr solutions. (P. Alexander, *Ann. N. Y. Acad. Sci.* **53**, 653 (1951), found supercontraction of wool in LiBr solutions.) No supercontraction was found. As may be seen in Figure 1, our fibers are fastened at both ends and would be forced to extend a spring if they contracted. The spring was weak, but it is within the realm of possibility that its retarding action was sufficient to reduce supercontraction to a negligible amount.

TABLE I. SWELLING OF HAIR IN NaBr SOLUTIONS

| Fraction of saturation | Concentration (mol./1000 g. water) | $[(V-V_w)/V_w]\times 100$ Hair #1 | Hair #2 |
|---|---|---|---|
| 0.1 | 0.7 | — | 1.9 |
| 0.2 | 1.5 | 1.7 | 2.4 |
| 0.4 | 3.2 | 4.0 | 3.5 |
| 0.6 | 5.1 | 4.5 | 3.5 |
| 0.8 | 7.0 | 4.0 | 3.2 |
| 1.0 | 9.1 | 3.8 | 3.0 |

TABLE II. SWELLING OF HAIR IN LiCl SOLUTIONS

| Fraction of saturation | Concentration (mol./1000 g. water) | $[(V-V_w)/V_w]\times 100$ Hair #1 | Hair #2 |
|---|---|---|---|
| 0.1 | 1.4 | 11.3 | 4.2 |
| 0.2 | 2.8 | 11.2 | 5.8 |
| 0.4 | 6.2 | — | 6.4 |
| 0.5 | 8.1 | 14.1 | — |
| 0.6 | 10.1 | — | 10.5 |
| 0.8 | 14.3 | 23.3 | 10.5 |
| 1.0 | 19.5 | 25.0 | 9.4 |

TABLE III. SWELLING OF HAIR IN LiBr SOLUTIONS

| Approximate fraction of saturation | Concentration (mol./1000 g. water) | $[(V-V_w)/V_w]\times 100$ Hair #1 | Hair #2 | Hair #3 |
|---|---|---|---|---|
| 0.1 | 1.2 | — | 2.6 | — |
| 0.2 | 2.6 | — | 4.5 | — |
| 0.4 | 5.7 | 7.6 | 7.1 | 4.1 |
| 0.6 | 9.0 | — | 23.0 | 16.7 |
| 0.8 | 13.0 | — | 26.9 | 22.7 |
| 1.0 | 17.7 | 30.1 | 28.8 | 23.6 |
| water | 0 | 7.1 | 7.9 | 5.6 |

As a reference, Stam [15, 16] found an average value of 32 ± 1% for the increase in volume of a hair on being transferred from the dry state to liquid water. The concentrations of the salt solutions are given as mol./1000 g. water, *m* (molality). The molarity obtained from analysis of the solutions or from the solubility was converted to molality with the use of density values taken from the International Critical Tables. The dependence of the equilibrium swelling on salt concentrations was found to be the following:

*NaCl*—No change in the water-swollen dimensions was found for a hair in NaCl solutions. (In view of the results using other alkali halides, these results should be checked.)

*KI*—A 1*m* solution of KI caused a 13.8% increase in volume. Solutions of higher concentrations reacted with the fiber, causing it to break.

*NaBr*—The swelling of two hairs in NaBr solutions is shown in Table I.

*LiCl*—The swelling of two hairs in LiCl solutions is shown in Table II.

*LiBr*—The swelling of three hairs in LiBr solutions is shown in Table III.

The results in Tables I and III are plotted in Figure 3. It is evident that the swelling power of LiBr is much greater than that of NaBr, although the two are comparable over most of the concentration range in which they overlap. It should be remembered that zero on the swelling axis corresponds to the water-swollen fiber. The greatest swelling shown in LiBr solutions corresponds to about 70%, based on the dry volume of the fiber.

The agreement between fibers for the swelling in LiCl and LiBr solutions is poor. Two causes possibly contributing to the discrepancies between fibers can be mentioned. In the first place, the water-swollen cross-sectional areas of the fibers used in the experiment with LiCl solutions are in the ratio 1 : 1.58, and those in the experiment with LiBr solutions in the ratio 1 : 1.26 : 1.46. The degrees of swelling decrease in the same order. It is thus possible that the finer fibers swell proportionately more. It is also known now that the absorption of LiBr from concentrated LiBr solutions is slow, as will be discussed in a future paper. It seems probable that the 24-hour swelling period is insufficient in a LiCl or LiBr solution at a concentration of 0.6 saturation or above. If equilibrium has not been obtained, it is to be expected that the drop below the equilibrium value will be most pronounced with the thickest fibers.

The results in Tables II and III have been taken by bringing the hair to equilibrium with dilute solutions of the respective salts, and then replacing these with successively more concentrated solutions.

When a water-swollen hair was immersed directly in a saturated LiCl solution, a 22.5% decrease in the cross-sectional area of the hair was found. (Drying of a water-swollen hair causes a decrease of about 25.6%.) The area of the hair was about the same as the area that would be found with a hair suspended over the LiCl solution (relative humidity 11.6%). Thus, immersion directly into a saturated LiCl solution apparently dries the fiber out, while the replacement technique causes increased swelling. This same phenomenon occurs with LiBr, and some further information on this effect can be obtained from Figure 4, which shows the volume change of a water-

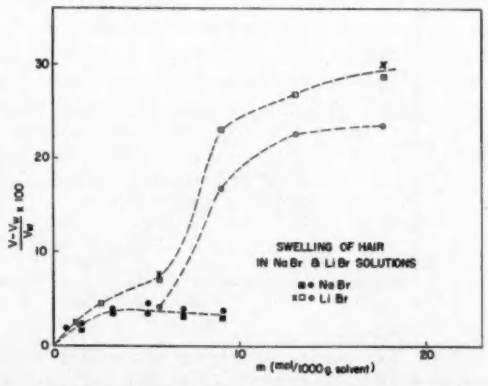


FIG. 3. *Swelling of hair in NaBr and LiBr solutions.*

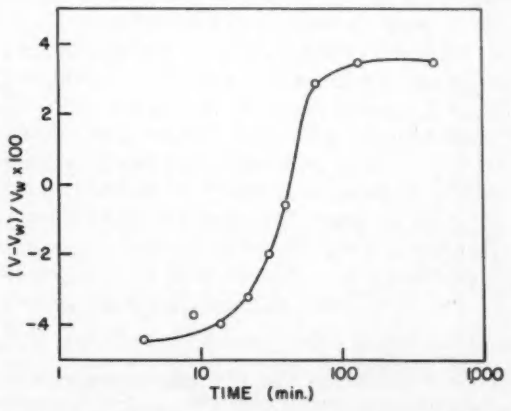


FIG. 4. *Rate of swelling of hair on transfer from water to a 5.7*m *LiBr solution.*

swollen hair immersed directly in a 5.7*m* LiBr solution as a function of time. At zero time the fiber is at zero on the ordinate. Thus, there is first a decrease in volume, and finally an increase. The behavior in LiBr or LiCl solutions can be explained in the following way.

When a water-swollen hair is immersed in a LiBr solution, water starts to diffuse out of the fiber, and salt to diffuse into it. The rate of diffusion of the salt is slower than that of the water and becomes slower as water is removed from the fiber. In a very concentrated solution so much water is removed from the fiber that the rate of diffusion of salt into it becomes infinitely slow, and the fiber is, in effect, dehydrated. In less concentrated solutions, the two opposing rates produce a minimum in the curve of swelling against time. These results were predicted by Burte [3] from consideration of experiments on the mechanical properties of hairs in salt solutions. Other measurements on the effect of LiBr solutions on the physical properties of hair have been reported by Hambraeus and Steele [5] and Steele [17]. In particular, Hambraeus and Steele found that the crystalline x-ray pattern of hair was destroyed by concentrated LiBr solutions when the hair was brought to equilibrium with the LiBr solution by the replacement technique.

The last row in Table III gives the swelling increases for hairs which have been transferred from saturated LiBr solutions to water. Hair #2 was left in water for five weeks. The rate of swelling recovery of hair #3 is shown in Figure 5. The initial degree of swelling is shown by the dotted line. A fairly rapid partial recovery is made, but a marked hysteresis of roughly 25% remains after a week in water.

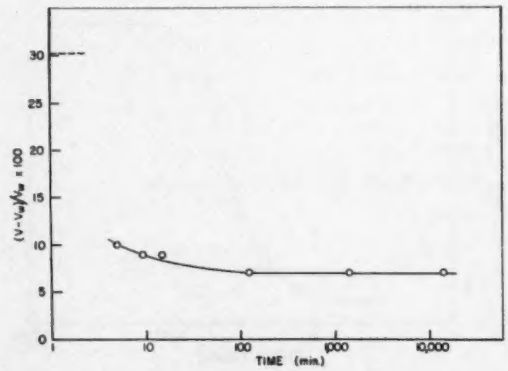


FIG. 5. *Rate of swelling recovery of hair on transfer from a saturated LiBr solution to water.*

*Swelling of Hair in HCl*

In Table IV and Figure 6 results are given for the swelling of hair in HCl solutions as a function of the pH of the solution. The pH values have been measured by means of a pH meter over the entire concentration range for hair #1 and down to pH 1 for the other hairs. The concentrations of the more acid solutions in the case of the other hairs were determined by titration. The pH values reported are negative logarithms of hydrogen ion concentration rather than pH-meter readings for the more acid

TABLE IV. SWELLING OF HUMAN HAIR IN HCl SOLUTIONS AT ROOM TEMPERATURE

| | $[(V-V_w)/V_w]\times 100$ | | | | |
|---|---|---|---|---|---|
| pH | Hair #1 | Hair #2 | Hair #3 | | Hair #4 |
| 4.5 | 0.6 | | | | |
| 4.0 | | | 0.3 | | 0.8 |
| 3.4 | 1.8 | | | | |
| 3.0 | | | 0.7 | | 1.9 |
| 2.5 | 1.5 | | | | |
| 2.0 | 2.1 | | 2.0 | 2.5 | 3.1 |
| 1.5 | 4.4 | | | | |
| 1.0 | 5.4 | 2.9 | 3.6 | 3.8 | 4.1 |
| 0.51 | | 2.1 | | 2.3 | 2.8 |
| 0.45 | 5.9 | | | | |
| 0.27 | | 1.7 | | 1.2 | 2.4 |
| 0.17 | 5.0 | | | | |
| 0.00 | | 2.1 | | 0.8 | 2.3 |
| −0.12 | 5.8 | | | | |
| 1.0 | | 3.1 | | 3.6 | |
| $H_2O$ | | | 0.0 | 0.2 | |

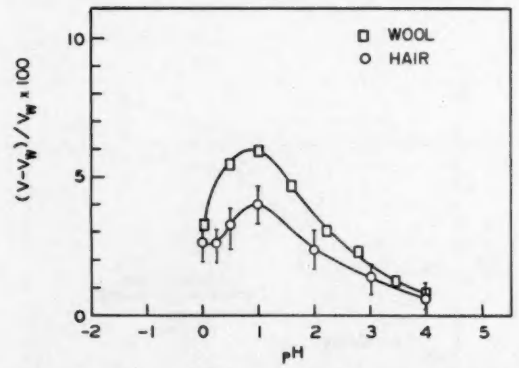


FIG. 6. *The swelling of keratin fibers in HCl solutions at room temperature. (The data for wool are from Speakman and Stott [14].)*

solutions. Below pH 1 there is a slight difference between the two, and the pertinent results for hair #1 contain a small correction [19]. The maximum correction is about 0.1 pH unit.

The results in Table IV were taken chronologically from top to bottom. Thus the last two rows represent desorption experiments and show that no swelling hysteresis occurs within the concentration limits set. The last row shows results in distilled water. The experiments in the second column for hair #3 followed those in the first.

An average curve of pH against swelling for the four hairs is given in Figure 6. Because of the differences between individual fibers and the shape of the pH-swelling curve, the curve shown can be taken to apply to pH measurements made with a pH meter with negligible increase in error. The second curve in Figure 6 shows results obtained by Speakman and Stott [14] for the swelling of wool in HCl solutions. A different microscopic technique was used, and the pH was determined with a pH meter. A measurement by Bogaty, Sookne, and Harris [2] on wool at pH 1 falls on the curve obtained by Speakman and Stott.

The difference between the curves for hair and for wool in the low pH region is somewhat surprising in view of the close chemical similarity between the two. Speakman and Elliott [13] found hair to absorb roughly 7% less HCl than wool from a solution of pH 2. However, this small decrease would not be expected to cause such a large decrease in swelling.

The cause of the increase in swelling above that of the water-swollen fiber can be examined by means of the following approximate calculation. Since the relative humidity of a 0.1$N$ HCl solution differs negligibly from that of water, the amount of water in the fiber can be set provisionally equal to the regain over liquid water. Thus for a hair (or wool fiber) in a 0.1$N$ HCl solution, the amount of water present within the fiber is 0.31 g./g. [4], and the amount of acid 0.8$mM$/g. [18]. The molarity of the "acid solution" in the hair is thus 2.45 mol./l. [6]. The apparent molal volume of HCl in water solutions, which is the increase per mole of acid added of the volume of the water phase on forming the solution, is given by the equation [7]:

$$\phi_V = 18.2 + 0.83\ C^{1/2},$$

which applies, strictly speaking, to more dilute solutions but should be accurate to the approximation desired here.

For a 2.45$M$ solution, this is 0.020 cc./$mM$ or 0.016 cc./g. dry fiber. This is the increase in volume per g. dry fiber to be expected when a water-wet fiber is transferred to a 0.1$N$ HCl solution. Since the density of dry wool (and presumably hair) is 1.31 g./cc. [10] and the volume increases by 1.31 : 1 on wetting [15], this is also $(V-V_W)/V_W$. The actual values, as seen from Figure 6, are 0.061 for wool and 0.04 for hair.

This calculation assumes that the HCl causes the same volume increase within the fiber that it causes in aqueous solution. The equation above shows that in aqueous solution the apparent molal volume is relatively insensitive to concentration changes and hence to small changes in environment. It seems unlikely that the apparent molal volume would increase two- or threefold in the hair. In fact, by analogy with water and other absorbates, a slight decrease in apparent molal volume might be expected. Thus, the discrepancy between the calculated and measured swelling values probably results from the assumption that the hair contains the same amount of water as in the water-swollen state. If more water is absorbed, either because of osmotic effects, as discussed by Procter and Wilson [11], or because the absorption of acid reduces the cohesive forces of the hair which resist swelling, the discrepancy is explained. Since most of the swelling is caused by water rather than by absorbed acid, it is possible for wool and hair to have different degrees of swelling for substantially the same acid content if the forces resisting swelling are different. Such a difference could result from different amounts of crystallinity or differences in morphology.*

TABLE V. SWELLING OF HAIR IN WATER AS A FUNCTION OF TEMPERATURE

| Temperature (°C) | $[(V-V_w)/V_w]\times 100$ |
|---|---|
| 40 | −0.2 |
| 50 | −0.4 |
| 67 | −0.6 |
| 78 | −0.6 |
| 93 | −0.8 |
| 93 (2 days later) | −0.9 |

* The reviewer noted that the cystine content of hair is greater than that of wool and that the resulting increase in concentration of sulfur cross-links would make hair more resistant to swelling. We agree that the increased cystine content is probably an important factor in explaining the lower swelling of hair. J. M. Lang and C. C. Lucas, *Biochem. J.* **52**, 84 (1952), give the cystine content of hair

*Effect of Temperature on the Swelling of Hair in Water*

In Table V some results are given on the effect of temperature on the swelling of hair in water. Speakman [12] examined the temperature dependence of the regain for wool. The regain decreases with increasing temperature at low relative humidities. At 95% R.H. a minimum is noted in the curve of regain against temperature at 45°C, the regain being about 7% lower than the regain at 25°C. Also, Speakman found that decomposition of the wool becomes appreciable at 50°C and above. The results in Table V show substantially no effect of temperature on the swelling of hair in water. No large changes in swelling occur with increased treatment at 93°C; however, swelling would not be expected to be a particularly sensitive measure of degradation. Since the measurements were made consecutively from top to bottom, it is possible that hysteresis in swelling recovery such as is found during solvent replacement masks a minimum which might be found by separate swelling experiments at 25°C and 50°C.

as 18.. g. amino acid/100 g. protein; S. R. Hoover, E. L. Kokes, and R. F. Peterson (TEXTILE RESEARCH JOURNAL 7, 423 (1948)) give the cystine content of wool as 12.72 g. amino acid/100 g. protein.

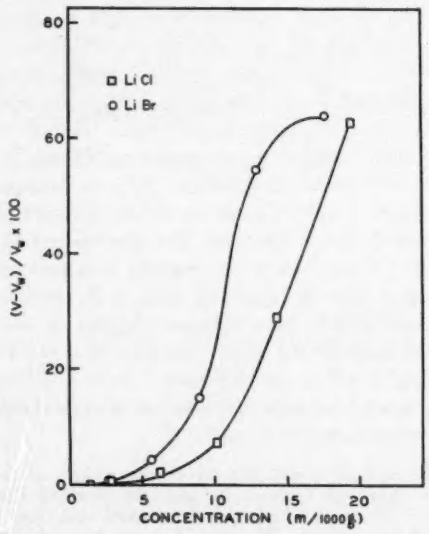


FIG. 7. *Swelling of rayon in LiCl and LiBr solutions at room temperature.*

*Swelling of Hair in a Dye Bath*

Finally, measurements were taken on the swelling of hair in a typical acid dye bath. The results are shown in Table VI. The first column runs chronologically from top to bottom. At each step one variable was changed until the final solution, which was a typical acid dye bath, was obtained. The dye used was Anthraquinone Blue SKY, Color Index Number 1088.

*Swelling of Cellulose*

The swelling of cellulose, regenerated by the viscose process, in aqueous salt solutions has been discussed by Usher and Wahbi [20] and by Kasbekar and Neale [8]. These workers used swelling to mean gross weight increase of treated sheets of cellophane rather than the volume change accompanying the increase. Since, in both cases, the composition of the cellulose phase was analyzed completely, the volume change of the cellulose could be calculated to a fair degree of accuracy by assuming appropriate partial molal volumes for the various absorbed components. However, since these workers used different salts and a different form of cellulose than were used for the work described herein, such a calculation for comparative purposes was not made.

The swelling which resulted when a dry viscose monofil was equilibrated with liquid water was determined to give some degree of characterization of

TABLE VI. SWELLING OF HAIR IN A DYE BATH

| History | $[(V-V_w)/V_w]\times 100$ |
|---|---|
| pH 2, room temperature | 2.1 |
| pH 2, 95°C | 2.7 |
| pH 2, 95°C, 0.53 g. NaCl / 400 cc. | 3.7 |
| pH 2, 95°C, 0.53 g. NaCl / 400 cc., 0.021 g. dye / 400 cc. | 7.4 |

TABLE VII. SWELLING OF VISCOSE IN LiCl SOLUTIONS

| Fraction of saturation | Concentration (mol./1000 g. water) | $[(V-V_w)/V_w]\times 100$ Fiber #1 | Fiber #2 |
|---|---|---|---|
| 0.1 | 1.4 | 0.2 | — |
| 0.2 | 2.8 | 0.7 | 0.4 |
| 0.4 | 6.2 | 3.3 | 0.7 |
| 0.6 | 10.1 | 8.9 | 5.5 |
| 0.8 | 14.3 | 28.5 | 29.9 |
| 1.0 | 19.5 | 65.6 | 60.6 |

the monofil used. This swelling was measured in the following way. A mounted monofil was dried over magnesium perchlorate in a vacuum desiccator for three days and then quickly removed and put into the cell, while the cell was being flushed with air previously passed through a drying train containing magnesium perchlorate as the last stage. The volume of the monofil was measured under these conditions and considered to be the dry volume. The cell was then filled with water, and after 24 hrs. the volume was measured. The water caused a 75.5% increase in area and a 4.0% increase in length. Subsequent solutions caused no further change in length.

*Swelling of Cellulose in Alkali Halide Solutions*

*NaCl.*—As was the case with hair, a saturated solution of NaCl caused the same degree of swelling as water. The same swelling was observed when a dry fiber was put into a saturated solution as when a water-swollen fiber was transferred to a saturated solution.

*KI.*—A saturated KI solution caused a 12.3% increase in volume over the water-swollen volume. All the increase was radial. When the fiber was washed with water for 24 hrs., 3.3% of the swelling remained, showing a hysteresis in the swelling-deswelling cycle.

*LiCl.*—The swelling of the viscose monofil in solutions of LiCl at room temperature is shown in Table VII and Figure 7. The curve for LiCl in Figure 7 is an average of the results for the two fibers. The results were obtained in descending order chronologically. However, contradistinct to hair, the same results can be obtained in a reasonable period of time by direct immersion even in very concentrated solutions. In the case of fiber #2, the saturated solution was replaced with water and the cell flushed with water periodically for a week. The swelling recovery was followed as a function of time, and is shown in Figure 8. The initial degree of swelling is shown by the dotted line. As with hair, as shown in Figure 5, a fairly rapid partial recovery is made followed by a slower process with the fiber remaining 10% larger than the water-swollen fiber after a week in water. The shape of the curve of Figure 8 suggests that the secondary recovery process is faster with the viscose monfil than with hair.

TABLE VIII. SWELLING OF VISCOSE IN LiBr SOLUTIONS

| Approximate fraction of saturation | Concentration (mol./1000 g. water) | $[(V-V_w)/V_w]\times 100$ Fiber #1 | Fiber #2 |
|---|---|---|---|
| 0.2 | 2.6 | 0.8 | — |
| 0.4 | 5.7 | 4.4 | 4.4 |
| 0.6 | 9.0 | 14.8 | 15.3 |
| 0.8 | 13.0 | 54.1 | 55.6 |
| 1.0 | 17.7 | 63.4 | 65.0 |

*LiBr.*—The swelling of the viscose monofil in LiBr solutions at room temperature is shown in Table VIII and Figure 7. Again the curve in Figure 7 represents an average of the results for the two fibers shown in Table VIII.

The results in Table VIII show that the action of LiBr is quite similar to that of LiCl, with slightly higher swelling at a given concentration occurring in the case of LiBr. As was true with LiCl solutions, the replacement method was not necessary in the case of viscose even when the treating solution was quite concentrated. If a swelling minimum such as is shown in Figure 4 existed, it was passed before it was possible to make the first measurement. Thus there is a basic difference between the hair and the rayon with respect to the rate of swelling, which suggests that the rayon monofil has a more open molecular structure than the hair. Whether this is true for more highly oriented rayons remains to be seen.

*Conclusions*

It may be concluded from the swelling results reported here that all of the solutions used are absorbed in appreciable quantities by both hair and viscose rayon with the possible exception of NaCl. Here absorption is used to denote any penetration

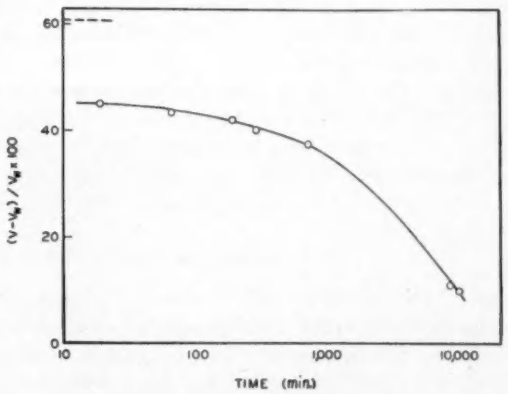


FIG. 8. *Rate of swelling recovery of rayon on transfer from saturated LiCl solution to water.*

within the fiber and not merely differential uptake with respect to water. Further analysis of the nature of the absorption depends on a knowledge of the amounts of water and solute absorbed by the fiber. The case of hair swollen with HCl has been discussed to some extent, and the action of NaBr and LiBr on hair will be treated in a further paper.

### Acknowledgment

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*(Manuscript received February 9, 1954.)*

# The Nature of the Hemicelluloses of Jute Fiber

## Part II*

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**Abstract**

Hemicellulose I from jute fiber has been subjected to periodate oxidation under different conditions. From the amount of formic acid liberated during the oxidation under optimum conditions and from its nonreducing character, it is suggested that hemicellulose I has a branched structure. Its molecular weight by the osmotic-pressure method has been found to be about 20,000.

Methylaldobiuronic acid, derived from hemicellulose I, gives both formic acid (2 mols.) and formaldehyde (1 mol.) on oxidation with periodate. It appears to be 3-(3-methylglucuronosyl)-*D*-xylose. Based on the observations made here, a provisional structure is suggested for hemicellulose I.

### Introduction

In a preliminary paper [18] from these laboratories, a very rough idea was given about the general nature of the hemicelluloses present in jute fiber. In Part I of this series [19] some details were published about the alcohol-insoluble hemicellulose I isolated from chlorite holocellulose of jute, and an approximate structure for the repeating unit, consisting of one monomethyluronic acid linked with six anhydroxylose groups, was suggested from the data then available. Hemicellulose I and methylaldobiuronic acid isolated therefrom have now been subjected to oxidation with periodate, and the consumption of periodate at different lengths of time, temperatures, pH's, etc., was measured in order to determine optimum conditions and the amounts of formic acid and formaldehyde liberated during the oxidation. The molecular weight of hemicellulose I, as its sodium salt, was determined by the osmotic-pressure method [1]. Its behavior towards alkaline 3:5-dinitrosalicylic acid was also studied. The results, which throw further light on the constitution of hemicellulose I, are described here.

Malaprade reaction with periodate, although apparently simple, gives rise to complications when applied to polysaccharides or polyuronides due to overoxidation or side-reactions. This has been observed by many workers, and modifications of the original procedure have been suggested [3, 7, 10]. The position is still somewhat obscure. It was therefore necessary to do some preliminary experiments to determine the conditions under which more or less concordant and reproducible results could be obtained with our product.

The colorimetric method of Meyer *et al.* [13] using 3:5-dinitrosalicylic acid was used to determine the reducing property of the hemicellulose; it has been shown [12] to give more reproducible results than other methods.

### Experimental

#### *Materials*

Hemicellulose I, employed in the present experiments, was isolated from the chlorite holocellulose of jute fiber and purified as in Part I [19]. The barium salt of methylaldobiuronic acid was obtained from hemicellulose I by acid hydrolysis, etc., and purified by repeated boiling under reflux with ethanol [19]. Sodium metaperiodate was prepared from sodium paraperiodate according to the method of Hill [8]; it was washed completely free from acid. 3:5-Dinitrosalicylic acid (m.p. 171°C) was obtained by the method of Sumner [22].

#### *Periodate Oxidation of Hemicellulose I*

A weighed quantity of the substance (about 1 g.) was put in an Erlenmeyer flask (250 ml.), thoroughly cleansed, and mixed with a definite volume of boiled-out distilled water (or buffer solution). The flask was shaken in a shaking machine for about 2 hrs. to obtain a colloidal solution, and cooled to 5°C if nec-

* Part I appeared in the August, 1952, issue, pp. 529–34.

TABLE I. EFFECT OF LIGHT, TEMPERATURE, AND pH ON THE PERIODATE OXIDATION OF HEMICELLULOSE I *

| Time (hrs.) | Moles of $IO_4^-$ consumed per 1,000 g. of hemicellulose I: At 5°C in dark | At room temp. (26°–32°C) in dark | At room temp. (26°–32°C) in presence of diffused sunlight | At 5°C in dark in buffer of pH 4.45† | At 5°C in dark in buffer of pH 7.09‡ | At 5°C in dark in buffer of pH 8.0‡ |
|---|---|---|---|---|---|---|
| 1 | 2.54 | 3.79 | 3.78 | 2.45 | 2.53 | 2.22 |
| 3 | 3.18 | 4.59 | 4.62 | 3.23 | 3.21 | 3.17 |
| 5 | 3.69 | 4.80 | 4.88 | 3.52 | 3.56 | 3.69 |
| 24 | 4.46 | 5.53 | 5.67 | 4.47 | 4.42 | 4.73 |
| 48 | 4.84 | 5.96 | 6.23 | 4.86 | 4.83 | 5.18 |
| 72 | 5.07 | 6.19 | 6.65 | 5.07 | 5.01 | 5.49 |
| 96 | 5.22 | 6.35 | 7.10 | 5.22 | 5.20 | 5.76 |
| 168 | 5.49 | 6.68 | 7.93** | 5.54 | 5.50 | 6.20 |
| 192 | 5.62 | 6.94 | — | 5.76 | 5.79 | 6.25 |
| 240 | 5.78 | 7.14 | — | 5.91 | 5.97 | 6.39 |
| 288 | 5.95 | 7.21 | — | 5.99 | 6.04 | — |

* Concentration of periodate was 0.1*M* in all cases. The total amount of periodate present in the reaction mixture was 8 moles per 1,000 g. of hemicellulose I.

† The buffer was prepared by mixing acetic acid and sodium acetate according to Walpole [2].

‡ The buffer was prepared by mixing borax and boric acid according to Palitzsch [2].

** $I_2$ was liberated.

TABLE II. EFFECT OF PERIODATE CONCENTRATION ON THE OXIDATION OF HEMICELLULOSE I *

| Time (hrs.) | Moles of $IO_4^-$ consumed per 1,000 g. of hemicellulose I: 0.05*M* | 0.1*M* | 0.15*M* | 0.2*M* |
|---|---|---|---|---|
| 1 | 1.58 | 2.54 | 3.16 | 3.34 |
| 3 | 2.31 | 3.18 | 3.87 | 4.16 |
| 5 | 2.61 | 3.69 | 4.16 | 4.41 |
| 24 | 3.70 | 4.46 | 4.78 | 4.96 |
| 48 | — | 4.84 | 5.12 | 5.22 |
| 72 | 4.42 | 5.07 | 5.33 | 5.44 |
| 96 | 4.56 | 5.22 | 5.49 | 5.56 |
| 168 | 4.87 | 5.49 | 5.80 | 5.82 |
| 192 | 4.97 | 5.62 | 5.89 | 5.90 |
| 240 | 5.18 | 5.78 | 6.04 | 6.02 |
| 288 | 5.30 | 5.95 | 6.19 | — |

* The reactions were conducted at 5°C in the dark, the amount of periodate being 8 moles per 1,000 g. of hemicellulose I in all cases.

TABLE III. EFFECT OF THE AMOUNT OF PERIODATE ON THE OXIDATION OF HEMICELLULOSE I *

| Time (hrs.) | Moles of $IO_4^-$ consumed per 1,000 g. of hemicellulose I: 8 moles/1,000 g. | 16 moles/1,000 g. | 24 moles/1,000 g. | 32 moles/1,000 g. |
|---|---|---|---|---|
| 1 | 2.54 | 2.67 | 2.73 | 2.86 |
| 3 | 3.18 | 3.31 | 3.34 | 3.42 |
| 5 | 3.69 | 3.93 | 3.97 | 3.98 |
| 24 | 4.46 | 4.68 | 4.84 | 4.84 |
| 48 | 4.84 | 5.12 | 5.13 | 5.19 |
| 72 | 5.07 | 5.37 | 5.48 | 5.54 |
| 96 | 5.22 | 5.63 | 5.61 | 5.71 |
| 168 | 5.49 | 5.98 | 5.99 | 6.22 |
| 192 | 5.62 | 6.16 | 6.13 | 6.41 |
| 240 | 5.78 | 6.24 | 6.34 | 6.57 |
| 288 | 5.95 | 6.33 | 6.43 | 6.60 |

* The reactions were carried out at 5°C in the dark and in 0.1*M* sodium metaperiodate solution in all cases.

essary. To this was added a measured volume of metaperiodate solution of known strength, also cooled to 5°C if necessary. The flask was shaken occasionally and kept in a refrigerator for oxidation at low temperature. For oxidation in the dark, the flask was covered with thick black paper. Five milliliters of the reaction mixture was taken out at intervals, and excess of periodate was determined according to the method of Fleury and Lange [4]. The results shown in Tables I, II, and III are the means of two or more observations.

It is seen from Figure 1 that 5 moles of periodate per 1,000 g. of hemicellulose I are consumed rather rapidly, and after that $IO_4^-$ consumption increases slowly, which may be due to overoxidation or side-reactions. At low temperature (5°C) in the dark and with a moderate concentration of periodate, the pH of the solution (if kept between 3 to 7) has little effect on the rate of periodate consumption. At room temperature (26°–32°C), and especially in the presence of light, the rate and over-all consumption of periodate increase. With greater amounts and concentrations of the oxidant, at low temperature in the dark, the periodate is consumed at a faster rate, but in all cases the figure for rapid consumption is practically the same—*viz.*, 5 moles per 1,000 g. of hemi-

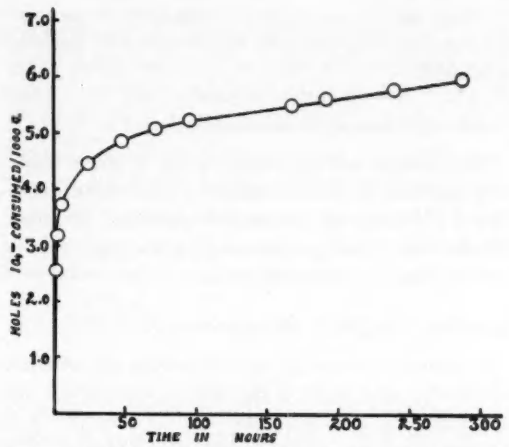



FIG. 1. *Periodate oxidation of hemicellulose I in 0.1M sodium metaperiodate solution at 5°C in the dark, with 8 moles of oxidant per 1,000 g. of hemicellulose I.*

cellulose. To follow up the oxidation of hemicellulose I with periodate, it seems desirable to carry out the oxidation at low temperature (say, 5°C) in the dark and in 0.1*M* periodate solution with a moderate excess of the oxidant.

*Determination of Formic Acid*

The procedure of Halsall *et al.* [6] was generally followed. The sodium salt of hemicellulose I (900 mg.) was put in an Erlenmeyer flask and shaken with 100 ml. of water to make a colloidal solution. To this was added 5 g. of potassium chloride and 25 ml. of 0.4*M* sodium metaperiodate solution. The oxidation was carried out at 10°–13°C in the dark. Five milliliters of the solution was withdrawn at intervals, 2 ml. of ethylene glycol (neutral) was added, and formic acid was estimated with 0.01*N* sodium hydroxide solution, using methyl red as indicator. The results, corrected according to Halsall *et al.* [6], are given in Table IV.

The liberation of formic acid was very slow after 120 hrs. The yield just after this period corresponds to one mole of formic acid per 5,000 g. of hemicellulose I. The same value is also obtained after 25 hrs. if the method of Potter and Hassid [16] is followed.

*Periodate Oxidation of Methylaldobiuronic Acid, $C_{12}H_{20}O_{11}$*

The barium salt of methylaldobiuronic acid (1.1341 g.) was dissolved in boiled-out, distilled water and

TABLE IV. FORMIC ACID OBTAINED FROM THE SODIUM SALT OF HEMICELLULOSE I BY PERIODATE OXIDATION

| Time (hrs.) | Moles of formic acid per 1,000 g. $\times 10^3$ |
|---|---|
| 1 | 2.25 |
| 5 | 4.48 |
| 25 | 6.11 |
| 48 | 10.96 |
| 96 | 17.52 |
| 120 | 20.42 |
| 150 | 21.94 |
| 180 | 24.45 |
| 216 | 26.85 |
| 288 | 30.84 |
| 388 | 31.28 |

TABLE V. PERIODATE OXIDATION OF METHYLALDOBIURONIC ACID *

| Time (hrs.) | $IO_4^-$ consumed | Moles of formic acid liberated |
|---|---|---|
| 0.25 | 2.41 | 0.76 |
| 1.00 | 2.95 | 0.98 |
| 2.50 | 3.25 | 1.14 |
| 5.00 | 3.63 | 1.24 |
| 27.00 | 4.18 | 1.80 |
| 48.00 | 4.52 | 2.01 |
| 72.00 | 4.82 | 2.32 |
| 96.00 | 5.41 | 2.70 |
| 120.00 | 5.68 | 2.87 |
| 192.00 | 6.09 | 3.26 |
| 240.00 | 6.24 | 3.28 |
| 360.00 | 6.50 | 3.88 |

* Figures expressed per mole of methylaldobiuronic acid.

treated with a slight excess of sodium sulfate to convert the acid to its sodium salt. The solution was filtered and made to 100 ml.

To 40 ml. of the solution, taken in a 250-ml. Erlenmeyer flask, 125 ml. of water was added, and the solution was cooled to 2°C. To the cooled solution was then added 25 ml. of 0.39*M* sodium metaperiodate solution. This solution was kept at 5°C in the dark. At intervals, 5 ml. of the solution (in duplicate) was taken out. In one, the excess periodate was determined by the method of Fleury and Lange [4], and in the other the formic acid liberated was determined according to Halsall *et al.* [6]. The results are given in Table V.

On standing, the neutralized solution slowly liberated more formic acid. This seems to arise from the hydrolysis of the formyl ester formed. Thus, after

27 hrs. another 0.15 mole of formic acid was liberated, making the figure 1.95.

It may be seen from Table V that in 27 hrs. 4 moles of periodate were consumed and 2 moles of formic acid were liberated per mole of methylaldobiuronic acid. No iodine was liberated even after 360 hrs. Formaldehyde was detected in the oxidized solution by Schryver's test [20]. Liberation of carbon dioxide was accelerated after the consumption of 4 moles of periodate per mole of the acid.

*Estimation of Formaldehyde*

Ten milliliters of a solution of the sodium salt of methylaldobiuronic acid (corresponding to 125.7 mg. of barium salt) was put into each of a number of 150-ml., stoppered, conical flasks, diluted with 25 ml. of water, and cooled to 5°C. To the cooled solution was added 5 ml. of ($N$) sodium bicarbonate and 6 ml. of 0.39$M$ sodium periodate solution. The flask was kept in the dark at 5°. At intervals, the contents of the flask were treated according to Reeves [17], with slight modification, to determine the amount of formaldehyde. The solution was acidified with 7 ml. of $N$ hydrochloric acid, and excess periodate was destroyed with $N$ sodium arsenite solution. The solution was then made alkaline with dilute sodium hydroxide (litmus paper). Ten milliliters of 8% dimedone in dilute sodium hydroxide was added, and the solution was acidified with acetic acid. The flask was kept overnight at 10°C in a refrigerator. The precipitate was filtered under mild suction in a glass filter and washed with water. It was dried at 105°C and weighed. The derivative melted at 187°–188°C (see Table VI).

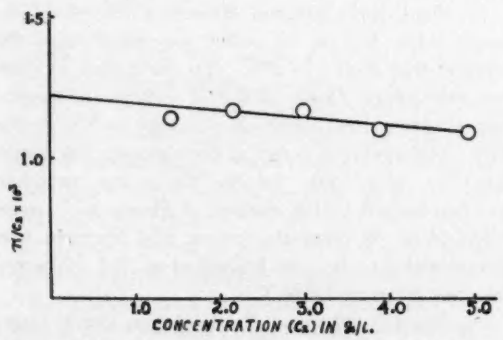



FIG. 2. *Osmotic pressure of the sodium salt of hemicellulose I in 0.4M sodium chloride solution.*

Thus, nearly one mole of formaldehyde per mole of methylaldobiuronic acid was liberated by periodate oxidation.

*Reducing Power of Hemicellulose I*

The sodium salt of hemicellulose I when treated with alkaline 3:5-dinitrosalicylic acid according to Meyer [13] appeared to be nonreducing. Therefore, this method of end-group assay is not applicable for determining the molecular weight of hemicellulose I.

*Molecular Weight of Hemicellulose I*

The molecular weight of the sodium salt of hemicellulose I, used in all of the above experiments, was determined by measuring the osmotic pressure of its solution in a Fuoss-Mead Osmometer [5] at 35°C in the presence of sodium chloride (0.4$M$) by the method of Bose *et al.* [1]. The results are given in Table VII and in Figure 2.

The intrinsic viscosity of the sodium salt of hemicellulose I in 0.4$M$ sodium chloride solution was found to be 0.0725, which corresponds to a D.P. of 66 using the constant $Km = 11 \times 10^{-4}$ employed by Millett and Stamm [14] for solution of aspen hemicellulose in water.

## Discussion

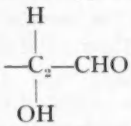
The liberation of formaldehyde from methylaldobiuronic acid by periodate oxidation indicates that the

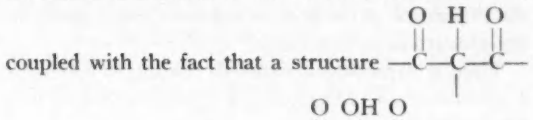
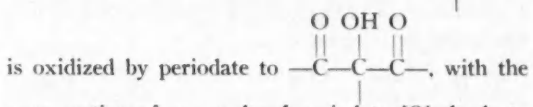
TABLE VI. YIELD OF FORMALDEHYDE FROM METHYLALDOBIURONIC ACID BY PERIODATE OXIDATION

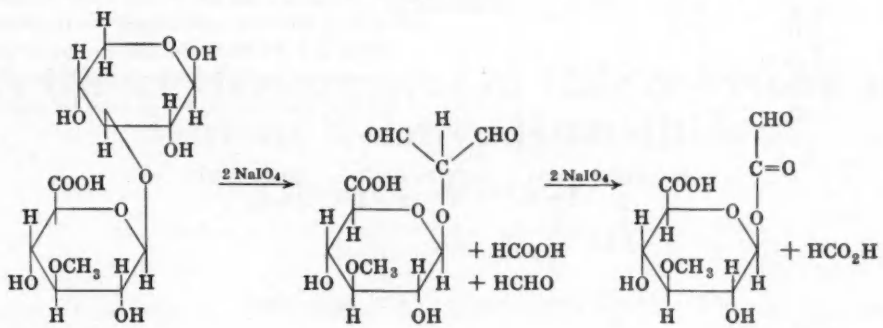
| Time (hrs.) | Mole of formaldehyde per mole of acid |
|---|---|
| 2 | 0.744 |
| 4 | 0.786 |
| 24 | 0.873 |
| 72 | 0.810 |

TABLE VII. MOLECULAR WEIGHT OF THE SODIUM SALT OF HEMICELLULOSE I

| Conc. ($C_2$) (g./l.) | $\pi$ (atm.$\times 10^3$) | $\frac{\pi}{C_2} \times 10^3$ | $(\pi/C_2)_{C_2=0} =$ R.T./$M$ | $M$ |
|---|---|---|---|---|
| 4.939 | 5.373 | 1.087 | | |
| 3.910 | 4.293 | 1.098 | $1.225 \times 10^{-3}$ | 20,640 (D.P. = 141) |
| 3.009 | 3.521 | 1.170 | | |
| 2.149 | 2.503 | 1.165 | | |
| 1.432 | 1.632 | 1.140 | | |

methyluronic acid residue is linked either to $C_3$ or $C_2$ of the xylose unit. The initial rate of liberation of formic acid from methylaldobiuronic acid from jute is found to be much faster than that (0.37 mole in 1.5 hrs.) from methylaldobiuronic acid from aspen wood hemicellulose [11]. The latter is described as 2-$\alpha$(4-methyl-*D*-glucuronosyl)-$\alpha$-*D*-xylose. In the present case, the acid residue appears to be attached to $C_3$ of the xylose unit;  group of xylose thus becomes available for periodate oxidation. The liberation of one molecule of formic acid from methylaldobiuronic acid within 1 hr. can thus be explained satisfactorily.

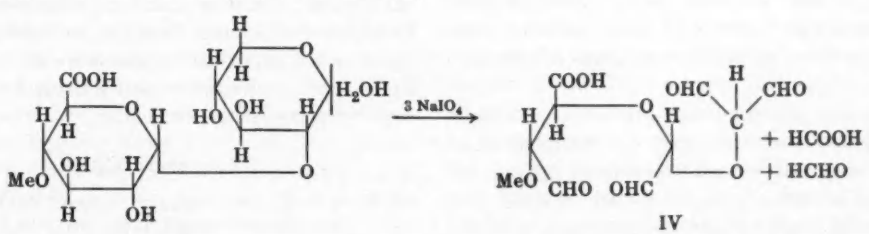
The consumption of 4 moles of periodate, with the liberation of 2 moles of formic acid, within 27 hrs., coupled with the fact that a structure  is oxidized by periodate to  , with the consumption of one mole of periodate [9], leads to the formulation of methylaldobiuronic acid as 3-(3-methylglucuronosyl)-*D*-xylose inasmuch as the occurrence of the methoxy group at $C_3$ alone will make the acid residue resistant to periodate oxidation.



I II

After the consumption of 4 moles of periodate, structure *I* is possibly converted into structure *II*, an ester of glyoxalic acid, which, being unstable in water, will hydrolyze slowly to glyoxalic acid and methylglucuronic acid [6]. Since glyoxalic acid is oxidized by periodate, with the formation of carbon dioxide [21] as one of the products of oxidation, the evolution of carbon dioxide from methylaldobiuronic acid from jute during periodate oxidation may be accounted for.

The methylaldobiuronic acid of structure *III* from aspen wood [11] is converted by periodate oxidation into structure *IV*,

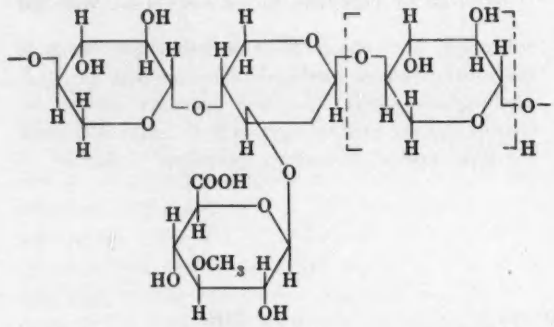


III IV

which, according to Pigman and Goepp [15], leads to the liberation of iodine. Jones and Wise [11] reported the liberation of iodine from aldobiuronic acid of aspen wood after 100 hrs., but no iodine was

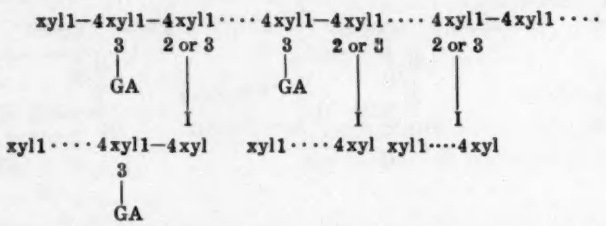
liberated from our product even after 336 hrs. This difference in the behavior of the two samples of methylaldobiuronic acid towards periodate, so far as liberation of iodine is concerned, may be due to the difference in the position of the methyl group in the glucuronic acid residue.

Thus, with methylaldobiuronic acid as 3-(3 methyl-*D*-glucuronosyl)-*D*-xylose, the repeating unit of jute hemicellulose I should be



By periodate oxidation, one mole of formic acid is obtained per 5,000 g. of the sodium salt of hemicellulose I. Four moles of formic acid would therefore result from one molecule of the sodium salt, having a molecular weight of about 20,000. Since the yield of formic acid obtained by the oxidation of nonreducing pentosan with periodate is a measure of the number of nonreducing end-groups, the jute hemicellulose molecule has 4 nonreducing end-groups or 3 branch points, the branches being attached by glycosidic bond to $C_2$ or $C_3$ of the xylose residue of the main chain.

The molecular weight of the sodium salt of hemicellulose calculated from the intrinsic viscosity of its solution in sodium chloride was found to be much less than that obtained from osmotic-pressure measurement. Although the value of the constant used in calculating the molecular weight from viscosity measurements is open to doubt, the low molecular weight thus obtained tends to support the branched formula of the hemicellulose I, which may be represented as




**Where xyl=xylose and GA=methylglucuronic Acid.**

The methylglucuronic acid (one in six xylose residue) may be connected to any one of the xylose units except the nonreducing terminal groups and the xylose units with the branching points.

Based on this structure, the hemicellulose I molecule (D.P. = 141) will consume 101 moles of periodate or 5 moles per 1,000 g. (7 units), which is actually obtained by periodate oxidation of hemicellulose I.

Some points regarding the structure of the hemicellulose I discussed here—*viz.*, (*i*) the mode of attachment of glucuronic acid residue to xylose, (*ii*) the position of methyl group in the acid residue, (*iii*) the number of nonreducing terminal groups, and (*iv*) the position of attachment of the branches to the xylose residues of the main chain—will have to be substantiated by isolating respective compounds after exhaustive methylation and hydrolysis. Work in this direction is in progress.


## Acknowledgment

Our thanks are due to Dr. S. R. Palit, Professor of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta, for kindly giving us facilities for osmometric measurements, and to Dr. P. K. Saha, Senior Research Assistant, for assistance in colorimetric measurements.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# A Direct Measurement of Hair Softening at Various Relative Humidities

**Dwight F. Mowery, Jr.***

*Contribution from the Department of Chemistry, Trinity College, Hartford, Connecticut*

THE direct measurement of the softening of human hair produced by water absorption has never been satisfactorily accomplished. Measurements of the tensile strength and elongation of hair yarns [3], Young's modulus [7], and the swelling of hair [5] at various humidities have been made. Also, the bending modulus of hair has been determined [2]. The object of the present investigation was the development of a reliable test method more closely associated with actual softening, which could provide a quantitative relationship between softening and increase in diameter, length, or volume so that, if desired, the softening could be calculated accurately from one of these geometric measurements. The most direct method of measuring true softening appeared to be the measurement of the force necessary to cut a hair with a sharp knife or razor blade. For fine human hairs of 0.05–0.07 mm. in diameter, forces of 7–12 g. were found necessary for severance of the solidly supported hair by a razor blade. By increasing the size of the torsion wire in an interfacial tensiometer and providing a holder for a razor blade and a plastic support for the hair, a very satisfactory instrument for measuring forces of this magnitude was devised.

## Experimental

### *Construction of Apparatus*

A Cenco-DuNouy precision interfacial tensiometer was modified as shown in Figure 1. The upper arm and vertical member holding the platinum ring were removed. The spring jaws for clamping the ring holder were replaced by a piece of Lucite $\frac{3}{8}$ in. thick. A no. 6 steel music wire of 0.016 in. diameter was substituted for the 0.011-in. wire furnished with the instrument. The force exerted at the end of the arm by this new wire was found to vary linearly with the tension readings up to readings of 200. Tension readings multiplied by the factor 0.0775 give the force in grams exerted by the instrument upon the razor blade. The razor blade, consisting of a small section of about $\frac{1}{4}$ in. edge and $\frac{3}{8}$ in. length broken from a standard double-edge razor blade, was

* Present address: Ripon College, Ripon, Wisc. This work was conducted at the request of Dr. Herbert H. Guest of the J. B. Williams Company.

held securely by means of a set screw in one end of a vertical slotted brass holder; the other end was fastened rigidly into the yoke at the end of the horizontal arm of the tensiometer. The counterweight originally on the end of the upper arm of the tensiometer was used on the lower arm to balance the razor blade and holder. In order to position the hair accurately under a given point of the razor blade edge, a ½-in. iron rod, holding at one end a small Lucite cutting platform ⅛ in. thick, was pivoted at the other end on a vertical iron post so that the cutting platform holding the hair could be swung under the razor blade. The iron post and tensiometer were solidly fixed with respect to each other by bolting both securely to a piece of ¾-in. plywood. In order to observe the placement of the hair under the blade, part of a low-power microscope (10 power eyepiece equipped with occular measuring scale and 5 power objective) including the focusing screw arrangement (not shown) was attached firmly to the tensiometer. A light, placed in back of and slightly above the tensiometer, silhouetted the blade and cast a shadow of it upon the cutting platform, thereby providing an accurate indication of the distance between the platform and the blade edge. In order to shield the eyes of the observer from the bright light behind the instrument, a shield (not shown) of appropriate size was placed over the upper end of the microscope tube. For regular increase in tension, which was found necessary for best results, the knurled knob intended for manual increase of tension was removed, and a pulley, belt, and small slow-speed motor controlled by a snap switch were substituted so that a regular increase of 200 scale divisions, or 15.5 g./min., was obtained.

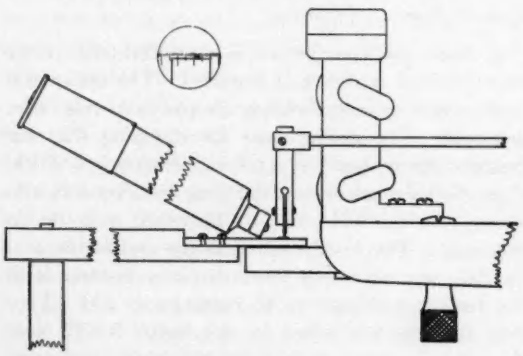

FIG. 1. *Equipment used for hair-cutting measurements. Inset shows positioning of hair segment at a definite point of the razor blade by means of the occular scale.*

*Operation of Apparatus*

The razor blade was adjusted in its holder so that its cutting edge was parallel to the Lucite cutting platform. The torsion wire was then adjusted by setting the tension scale reading at zero, releasing the lower arm stop, and bringing the razor blade just to rest on the cutting platform by means of the knurled screw at the end of the torsion wire opposite the calibrated dial. This adjustment was usually necessary only once at the start of a series of 20 cutting trials, provided cutting tensions did not exceed 150 scale divisions. The hair was placed for cutting by raising the blade by means of the lower arm stop, swinging back the iron rod, carefully lining up the hair section on the platform by means of small tweezers, and again returning the rod and platform to the original position under the razor blade. The final exact position could readily be obtained by gently tapping the iron rod while observing the hair position on the microscope scale (inset of Figure 1) and at the same time slowly lowering the razor blade by means of the lower arm stop. For convenience in reading the scale, the hair sections were generally located 10 or 20 divisions from either edge of the blade. To cut the hair, the motor was switched on and at the moment the blade cut through the hair, usually with a visible snap, it was switched off again; the tension was read from the scale. If the motor has appreciable inertia, a constant correction must be subtracted from each tension reading. The tensiometer was then returned to zero by manually backing up the pulley on the tensiometer. In order to accomplish this and also reduce friction on the tensiometer bearings, the belt should not be too tight.

*Data Obtained*

Twelve brown washed female human hairs of reasonably uniform diameter, as measured with a 440 power microscope equipped with an occular scale and micrometer stage, were selected, and each was cut into twenty ⅛-in. sections. Alternate sections of a given hair were placed in order upon two metal plates, each plate being ruled into 10 squares for locating the hair segments. Both plates were then placed in a vacuum desiccator containing $P_2O_5$ for 1 week in order to dry the hair completely, so that water would subsequently be regained rather than lost.

The plates were then removed, and each was placed for 2 weeks in a desiccator at a given relative humidity maintained by sulfuric acid solutions of different concentrations [6]. The hair sections were removed one at a time, alternately, from the two desiccators and cut at 50 ± 5% room humidity in the same order as they occurred in the original hair, starting at the root and working towards the tip of the hair. The cutting operation usually required between 1 and 2 min., including the time necessary to remove the hair from the desiccator and place it in position for cutting. The only difference in the treatment of the two groups of hair sections was the relative humidity at which each group was kept for 2 weeks prior to cutting, and thus a relationship was established between softening, as measured by ease of cutting, and water content of the hair, determined by the humidity. Alternate sections of a given hair were kept at the following pairs of relative humidities: 0% and 10%, 10% and 25%, 25% and 35%, 35% and 50%, 50% and 65%, 65% and 75%, 75% and 90%, 90% and 100%. Also compared were hair segments at the following pairs of humidities: 10% and 50%, 25% and 50%, 75% and 50%, and 90% and 50%. The results of these 240 cutting trials are given in Table I.

*Calculations*

The difference between each pair of tension averages for a given set of cutting trials listed in the last column of Table I is expressed as a percentage of the average tension at the humidity listed as the comparison humidity in column 4 of Table II. This figure is tabulated in column 5 of Table II as % softening based on comparison humidity. The errors accompanying these figures are standard errors calculated in the usual way [4] from the following formula:

$$\text{standard error} = \sqrt{\frac{\sum (x - \bar{x})^2}{N(N-1)}} = \sqrt{\frac{\sum (x - \bar{x})^2}{10 \times 9}} = 0.105 \sqrt{\sum (x - \bar{x})^2},$$

where $x$ = % softening based on the comparison humidity for each consecutive pair of cutting trials, $\bar{x}$ = average of 10 values for $x$ obtained from the 20 cutting trials, $N$ = number of $x$ values averaged (10 in these experiments), and $N - 1$ = degrees of freedom, used instead of $N$ for small samples. In column 6 of Table II is given the partial % softening based on dry hair, calculated from the figure in the preceding column ($x$ below) and the figure in column 7 of the preceding trial for sets 2–8 or 13.1

TABLE I. TENSION MEASUREMENTS FOR INDIVIDUAL CUTTING TRIALS

| Set No. | R.H. (%) | Individual tension readings from instrument* | | | | | | | | | | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 142 | 145 | 148 | 143 | 147 | 147 | 133 | 130 | 134 | 144 | 141.3 |
| | 10 | 142 | 148 | 145 | 145 | 145 | 140 | 134 | 132 | 137 | 143 | 141.1 |
| 2 | 10 | 168 | 160 | 150 | 165 | 163 | 158 | 174 | 183 | 171 | 175 | 166.7 |
| | 25 | 156 | 148 | 145 | 150 | 148 | 165 | 156 | 180 | 183 | 169 | 160.0 |
| 3 | 25 | 115 | 121 | 108 | 111 | 107 | 103 | 111 | 120 | 137 | 128 | 116.1 |
| | 35 | 110 | 110 | 100 | 110 | 114 | 107 | 116 | 114 | 125 | 125 | 113.1 |
| 4 | 35 | 127 | 138 | 135 | 138 | 123 | 123 | 115 | 122 | 115 | 123 | 125.7 |
| | 50 | 121 | 128 | 116 | 128 | 118 | 123 | 106 | 106 | 105 | 118 | 116.9 |
| 5 | 50 | 101 | 104 | 93 | 89 | 83 | 78 | 81 | 85 | 96 | 97 | 90.7 |
| | 65 | 85 | 82 | 83 | 81 | 73 | 74 | 71 | 80 | 89 | 89 | 80.7 |
| 6 | 65 | 102 | 108 | 100 | 104 | 105 | 106 | 110 | 98 | 105 | 105 | 104.3 |
| | 75 | 101 | 103 | 95 | 90 | 102 | 101 | 108 | 91 | 93 | 103 | 98.7 |
| 7 | 75 | 105 | 104 | 114 | 103 | 102 | 100 | 109 | 110 | 109 | 108 | 106.4 |
| | 90 | 100 | 98 | 103 | 93 | 98 | 96 | 105 | 97 | 98 | 97 | 98.5 |
| 8 | 90 | 115 | 111 | 113 | 117 | 116 | 116 | 113 | 107 | 105 | 100 | 111.3 |
| | 100 | 119 | 110 | 116 | 113 | 120 | 118 | 108 | 98 | 100 | 103 | 110.5 |
| 9 | 10 | 160 | 167 | 148 | 156 | 161 | 165 | 166 | 150 | 141 | 135 | 154.9 |
| | 50 | 143 | 148 | 138 | 132 | 137 | 136 | 152 | 126 | 125 | 120 | 135.7 |
| 10 | 25 | 144 | 156 | 143 | 133 | 153 | 164 | 167 | 170 | 172 | 174 | 157.6 |
| | 50 | 138 | 146 | 132 | 124 | 149 | 151 | 152 | 155 | 148 | 155 | 145.0 |
| 11 | 75 | 76 | 69 | 71 | 66 | 72 | 66 | 70 | 72 | 67 | 73 | 70.2 |
| | 50 | 86 | 82 | 78 | 76 | 86 | 83 | 87 | 87 | 76 | 86 | 82.7 |
| 12 | 90 | 105 | 94 | 95 | 90 | 100 | 93 | 90 | 81 | 90 | 90 | 92.8 |
| | 50 | 128 | 116 | 120 | 122 | 126 | 123 | 118 | 98 | 108 | 113 | 117.2 |

* Instrument readings can be converted to grams by the use of the multiplier 0.0775.

from set 4 for sets 9–12 ($y$ below) by means of the following expression:

partial % softening based on dry hair $= x - xy/100$ (at test humidity relative to comparison humidity)

where $x$ = % softening at test humidity relative to and based on the comparison humidity, and $y$ = % softening at the comparison humidity relative to and based on the dry hair.

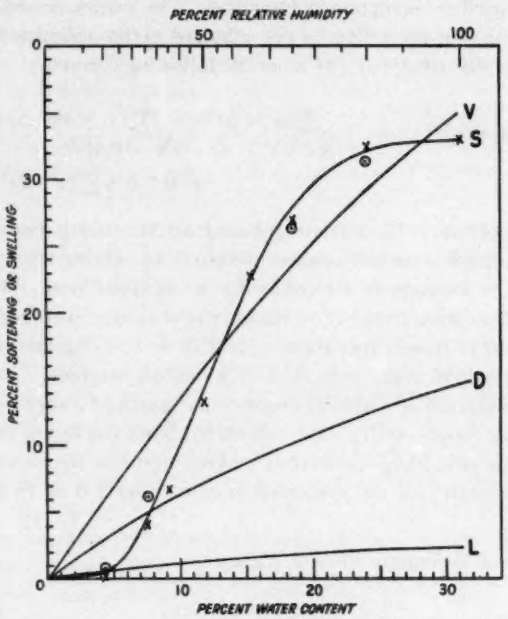


FIG. 2. *Curves showing softening* (S), *increase in volume* (V), *increase in diameter* (D), *and increase in length* (L) *of human hair upon absorption of water.*

This relationship is derived as follows: $a$ = tension necessary to cut the dry hair, $b$ = tension necessary to cut the hair at the comparison humidity, and $c$ = tension necessary to cut the hair at the test humidity. Then

$$x = 100(b - c)/b$$

and

$$y = 100(a - b)/a.$$

From these two equations and the above definitions the following pair of relationships are derived:

partial % softening based on dry hair
$= 100(b - c)/a = x - xy/100$
(at test humidity relative to comparison humidity)

total % softening based on dry hair
$= 100(a - c)/a = x + y - xy/100$
(at test humidity relative to dry hair)

This last quantity is tabulated in column 7 of Table II. It should be noted that in calculations for set 1, $y = 0$, since the comparison humidity for this set is dry hair. In order to obtain curve $S$ in Figure 2, the values of column 7 were plotted against water content of the hair determined from the relative humidity by means of the data of Chamberlain and Speakman [1]. An S-shaped curve was obtained.

## Discussion of Results

Although the standard errors of the partial softenings are quite large compared to the measured quantities, it is believed that the standard errors of the

TABLE II. VARIATION OF HAIR SOFTENING WITH HUMIDITY

| Set No. | Hair diameter* | Test humidity (%) | Comparison humidity (%) | % Softening based on: Comparison humidity | Dry hair: Partial | Dry hair: Total† |
|---|---|---|---|---|---|---|
| 1 | 20–25 | 10 | 0 | 0.1 ± 0.7 | 0.1 ± 0.7 | 0.1 |
| 2 | 19–25 | 25 | 10 | 4.0 ± 1.8 | 4.0 ± 1.8 | 4.1 |
| 3 | 21–25 | 35 | 25 | 2.6 ± 1.9 | 2.5 ± 1.8 | 6.6 |
| 4 | 17–21 | 50 | 35 | 7.0 ± 1.3 | 6.5 ± 1.2 | 13.1 |
| 5 | 16–22 | 65 | 50 | 11.0 ± 1.5 | 9.6 ± 1.3 | 22.7 |
| 6 | 20–25 | 75 | 65 | 5.4 ± 1.3 | 4.2 ± 1.0 | 26.9 |
| 7 | 16–19 | 90 | 75 | 7.4 ± 1.0 | 5.5 ± 0.7 | 32.4 |
| 8 | 22–25 | 100 | 90 | 0.7 ± 1.3 | 0.5 ± 0.9 | 32.9 |
| 9 | 21–24 | 10 | 50 | −14.2 ± 1.4 | −12.4 ± 1.2 | 0.7 |
| 10 | 18–23 | 25 | 50 | − 8.0 ± 1.0 | − 7.0 ± 0.9 | 6.1 |
| 11 | 19–24 | 75 | 50 | 15.1 ± 1.1 | 13.1 ± 1.0 | 26.2 |
| 12 | 19–23 | 90 | 50 | 20.8 ± 1.0 | 18.1 ± 0.9 | 31.2 |

* Hair diameters are given in ocular scale units, and can be converted to millimeters by the use of the multiplier 0.00275.
† % Softening that would be experienced by a completely dry hair if kept for 2 weeks at the relative humidity of column 3.

sums of these partial softenings, which are plotted in Curve *S* of Figure 2, are not appreciably greater than the errors of the individual quantities themselves, which amount to hair softenings of about 1%–2%. Evidence for this comes from the agreement of sets 9–12 (circles in Figure 2) with the previous eight sets (*x's* in Figure 2), whose results were summed. It is to be noted that the points for sets 9 and 10 fall slightly above the curve representing the previous sets, and those for set 11 and 12 occur slightly below. This would be expected if a slight absorption of water took place during cutting of the hair segments at 10% and 25% humidity, and if a slight loss of water took place during cutting of the segments at 75% and 90% humidity, the comparison segments being at 50% humidity, the same as the room, and therefore neither gaining nor losing water. The gain or loss of water during cutting in sets 1–8 should be almost equal for the two groups of segments compared, and therefore introduce little error since the relative humidities did not differ by more than 15%. By increasing the number of cutting trials in each set, the standard errors could be reduced considerably—for example, increasing the number of cutting trials per set threefold would reduce the standard error by approximately two thirds. The extra labor involved was not considered worth while in the present investigation.

The shape of the curve obtained (curve *S* in Figure 2) indicates that water absorption causes less softening at both low (below 25%) and high (above 75%) relative humidities than it does at intermediate humidities. At humidities between 25% and 75%, the relationship between softening and water absorbed is approximately linear, the % softening being about 2.3 times the % water absorbed. These results should be interpreted as indicating that binding forces, at least longitudinal ones, in human hair are weakened by water absorption to the greatest extent for hair between 25% and 75% relative humidity and to a smaller extent for hair below 25% or above 75% relative humidity.

For comparison with the softening curve *S* in Figure 2, there are plotted from the data of White and Stam [5] curves *V*, *D*, and *L* representing, respectively, the percentage increase in volume, diameter, and length of human hair at given relative humidities or water contents. It is evident that the softening does not parallel any of these three quantities exactly, but is closer to % increase in volume than the others. The % increase in volume at 50% relative humidity is approximately 1.2 times the % water absorbed, which means that at this humidity the % softening is about 2.3/1.2, or 1.9 times the % increase in volume. Figure 2 can be used very conveniently for interconversions of % change in volume, diameter, or softening of human hair due to variation of humidity or water content. If interconversions involving % change in length are required, a plot of this quantity on ten times the scale of Figure 2 is more convenient.

## Summary

An interfacial tensiometer has been adapted to measure the force which must be applied to a sharp razor blade to cut a single human hair. The relationship between softening, as measured in this way, and the water content of the hair at different humidities can be represented by a sigmoid curve. A graph is presented which relates softening of hair by water to changes in various geometric measurements of the hair.

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# Properties of Apparel Wools

## VI. Aging of Top and Roving Produced on the French Worsted System*

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**Abstract**

The aging of top and roving produced on the French worsted system has been investigated by measuring the dimensional changes and the mechanical properties of these fiber assemblies. The experimental results indicate that one consequence of aging is a relaxation of stresses in the fibers caused by deformation of the fiber crimp during previous processing. A brief high-temperature, high-humidity treatment of the top balls or roving bobbins has many of the same effects on the properties of the top and roving as a long aging period at 65% R.H. and 70° F.

### Introduction

There is a widespread belief among worsted manufacturers that aging top prior to drawing and aging roving prior to spinning may have beneficial effects on the drawing and spinning. The top balls or roving bobbins may be aged for a period of one week to several months; the atmospheric conditions during this aging are often about 70% R.H. and 70°F. There is no good agreement as to optimum aging conditions.

The aging of top and roving has been studied by workers at the Wool Industries Research Association. They state that "the storage of wool at a high regain is generally considered to have a beneficial effect on subsequent processing," [8] and that "it is also general practice, when deliveries of top from the wool comber have been made to the worsted spinner, for the latter to store them for weeks or even months in a convenient shed or cellar to allow them to 'set'. This is generally said to promote relaxation of the fibres and the removal of those strains in them imposed during carding and combing" [9]. They comment on the nature of these strains: "The crimp of fibres in tops is very small compared with that in the fibres before combing. It is assumed that this loss of crimp is due to the application of moisture and heat to the wool during combing, and to the fibres being constantly under tension until they are finally made into tops. During storage, it is generally believed that the fibres acquire a temporary set while they are in this tensioned state, and that the crimp does not return" [10]. They measured the drag necessary to pull apart samples of slivers as a function of time of storage [11], and found that for slivers with no added oil there was no appreciable change of the drag with time of storage. For slivers containing 0.9% to 4.5% added oil the drag did change with time of storage, and this they attributed to oxidation of the oil films on the fibers.

Speakman and coworkers have also studied the aging of top [5, 6] and state that ". . . the fibres have been strained in gilling and combing by removal of crimp and actual extension. . . . If tops were processed immediately after manufacture, the fibres would tend to contract and resume their crimped form, thus interfering with yarn manufacture. By storing the tops opportunity is given for the tension within the fibres to decay." These investigators found that the force necessary to pull apart samples of unoiled top increased with time of storage, and they give the following as an explanation: "As the storage time is increased the fibres tend to preserve the

* A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Western Utilization Research Branch of the Agricultural Research Service. Other phases of the project are sponsored by the American Wool Council; the International Wool Secretariat; the National Wool Trade Association; the Office of Naval Research, Department of the Navy; and by a number of American wool manufacturers.

Parts I-V appeared in the Feb., 1952, July, 1952, July, 1953, Oct., 1953, July, 1954, issues, respectively. Part VII appears in this issue, p. 726.

† At present on active duty in the United States Air Force.

straight form during testing, and the total friction within a top is increased on account of more effective fibre to fibre contact"—*i.e.*, there is "an increasing failure of the fibres to recover the crimped form when a length of top is withdrawn for testing." When oiled tops were stored additional effects, attributed to oxidation of the oil films, were found to occur.

Barritt [2] also found that the force necessary to pull apart samples of oiled tops increased with time of storage. Anderson, Cox, and Hardy [1] suggested that during the storage of slivers adhesions may be set up between the fibers.

One of the tasks undertaken on the Wool Research Project * was a further investigation of what, if anything, happens to the top or roving during the aging period. The problem was attacked in two ways: properties of single fibers withdrawn from the top and roving were measured, and properties of the whole fiber assemblies were measured. The results of the single fiber studies were presented in the preceding paper in this series [4]. The present paper describes the results of the assembly measurements and presents a more detailed discussion than was heretofore available of the several processes that may occur during aging.

## Experimental

The tops and rovings used in these experiments were produced on the French worsted system and had no net twist. Some of their physical characteristics are listed in Table I. The tops contained no added oil; the rovings contained a small amount of peanut oil added in the form of an emulsion at the start of the drawing. The tops were wound into balls and the rovings into double-meche bobbins. Sample top balls and roving bobbins were placed in a conditioned room, maintained at 65% R.H. and 70°F, within a few hours after processing. These samples are referred to as normal top or roving.

The first series of experiments indicated that one consequence of aging was a relaxation of stresses in the fibers caused by previous processing. Since it was expected that heat and moisture would accelerate such a relaxation process, several freshly made top balls and roving bobbins were subjected to a short "steaming" treatment before being placed in the conditioned room. This steaming was carried out in equipment normally used for setting the twist in woolen and worsted yarns and consisted of the following cycle: 5 or 10 min. heating, 5 or 10 min. at constant conditions, 5 or 10 min. cooling. During the constant period the atmospheric conditions in the steam chest were: dry bulb temperature = 183°–185°F, wet bulb temperature = 178°–180°F, and normal atmospheric pressure. The top balls were subjected to from one to three such cycles, the roving bobbins to one cycle. Top or roving treated in this way is referred to as steamed top or roving.

It should be emphasized that the steamings just described and the agings of both the steamed and normal tops or rovings were performed on tops or rovings that were constrained by being wound onto a top ball or roving bobbin. With rare exceptions, atmospheric conditions during the aging period were maintained at 65% R.H. and 70°F.

Two types of experiment were performed: one was concerned with the dimensional stabilities of strands of top or roving, the other with the mechanical properties of these fiber assemblies.

### *Dimensional Stability Experiments with Top*

*Dimensional changes due to unwinding recovery.*— The unwinding of a strand of top from an unaged normal ball caused a pronounced lateral expansion of the strand which will be referred to as the unwinding

TABLE I. PHYSICAL PROPERTIES OF WOOL TOPS AND ROVINGS

| | Weight per unit length (g./m.) | Average fiber fineness (μ) | Average fiber length (in.) | Content of ether extractable material (%) |
|---|---|---|---|---|
| | | *Tops* | | |
| Australian fine | 20 | 19.8 | 2.4 | 0.22 |
| U. S. fine | 20 | 21.8 | 2.8 | 0.44 |
| U. S. medium | 20.1 | 26.5 | 3.2 | 0.57 |
| New Zealand medium | 20 | 26.2 | 3.2 | 0.90 |
| | | *Rovings* | | |
| Australian fine | 0.21 | 19.8 | 2.46 | 0.40 |
| U. S. fine | 0.21 | 21.6 | 2.88 | 0.82 |
| U. S. medium | 0.21 | 26.2 | 3.35 | 0.84 |
| New Zealand medium | 0.21 | 26.1 | 3.33 | 1.24 |

* The Wool Research Project was concerned with an evaluation of the properties and processing of four wools: an Australian 70's grade Merino, a New Zealand 58's grade crossbred, a U. S. 64's grade Rambouillet, and a U. S. 58's grade crossbred. A summary of the processing operations was given in the first paper of this series [7].

recovery. The width of the strand was found to increase by as much as 20% due to this type of recovery. Unfortunately, no data were obtained for a reliable comparison between the unwinding recoveries for top strands from unaged normal balls and from aged normal balls. The top from unaged steamed balls showed little or no unwinding recovery.

*Dimensional changes due to crimp recovery.*—After discarding the outer layer of the top ball, samples approximately 20 in. in length were removed from the ball, and were placed on a smooth horizontal surface under atmospheric conditions maintained at 65% R.H. and 70°F. One end of the sample was clamped to the surface; otherwise the samples were free of winding constraints. Their dimensions were then measured as a function of time after removal from the ball. The results presented in Figures 1, 2, and 3 show that samples removed from unaged normal top balls increased in width and decreased in length. In these figures the lengths and widths are expressed relative to the lengths and widths at the time of the first measurement (5 to 15 min. after removing from the ball). Visual inspection indicated that, as these dimensional changes of the whole fiber assembly occurred, the crimp configuration of the individual fibers showed pronounced changes. These dimensional changes are considered to be due to a crimp recovery. It should be noted that the recovery due to unwinding described in the preceding section had already taken place by the time of the first measurements.

Similar experiments on dimensional stability were performed on samples of aged normal top and of unaged steamed top; these results are presented in Figures 2 and 3. The dimensional changes for these samples were much smaller than were those for samples of unaged normal top.

*Effect of removal of electrical charge on the dimensional changes due to crimp recovery.*—Since there was a possibility that the dimensional changes attributed to crimp recovery were partially caused by an electrical charge on the fibers, the dimensional changes were also measured for a sample of unaged normal top which was first exposed to radiation from a radium foil to allow any static charge to be dissipated. The results, given in Figure 4, show that the static removal treatment did not significantly affect the dimensional changes.

*Effect of relative humidity on the dimensional changes due to crimp recovery.*—The dimensional changes due to crimp recovery were increased in rate and extent by raising the relative humidity of the atmosphere to which the samples were exposed.

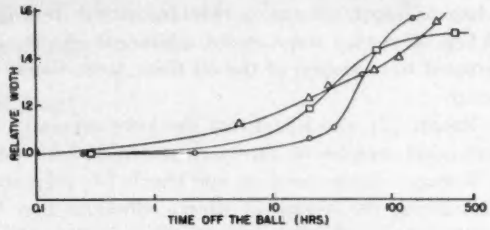


FIG. 1. *Dimensional changes of unaged normal top.* ○—*U. S. fine wool;* △—*U. S. medium wool;* □—*New Zealand medium wool.*

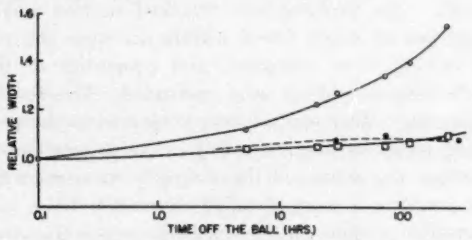


FIG. 2. *Dimensional changes of top made from the U. S. medium wool.* ○—*Unaged normal top;* ●—*Aged normal top;* □—*Unaged steamed top.*

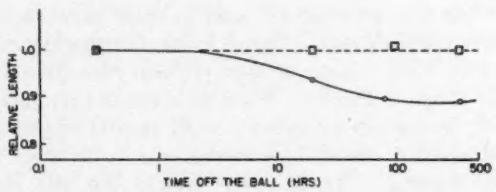


FIG. 3. *Dimensional changes of top made from the New Zealand medium wool.* ○—*Unaged normal top;* □—*Unaged steamed top.*

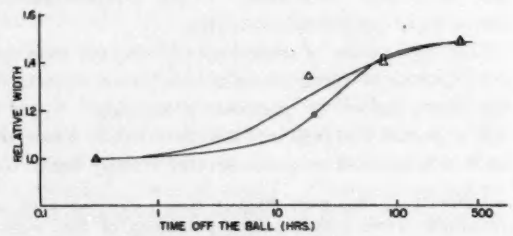


FIG. 4. *Dimensional changes of unaged normal top made from the New Zealand medium wool.* ○—*No static removal treatment;* △—*Static removal treatment.*

The data in Table II show that, for a sample of unaged normal top, 255 hrs. at 65% R.H. caused an increase in strand width of 55%, whereas only 9 additional hours at a relative humidity greater than 95% caused a further increase of 58% in width. The corresponding values for a sample of unaged steamed top were 10% and 11%. The difference in the widths of the samples of unaged normal top and unaged steamed top at 0.1 hr. was probably due to the lack of an unwinding recovery with the latter sample.

TABLE II. THE EFFECT OF RELATIVE HUMIDITY ON THE DIMENSIONAL STABILITY OF TOP MADE FROM THE U. S. MEDIUM WOOL

| Time of measurement of width | Sample width (in.) Unaged normal top | Unaged steamed top |
|---|---|---|
| 0.1 hr. after removing from ball | 1.83 | 1.42 |
| After 255 hrs. at 65% R.H. and 70°F | 2.86 | 1.57 |
| After 9 additional hrs. at 95% R.H. and 70°F | 3.93 | 1.73 |

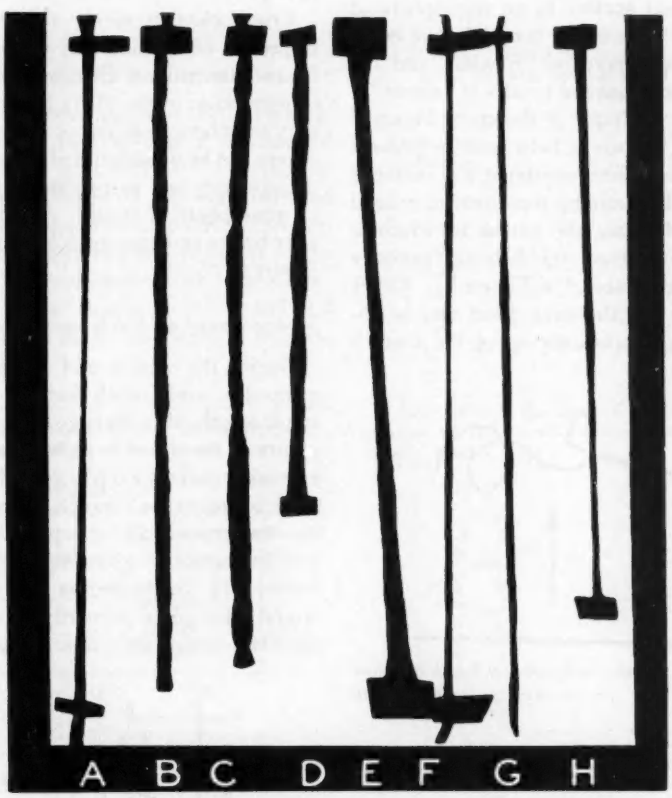


FIG. 5. *Dimensional changes of roving.* (*These illustrative samples not made from a Wool Project wool.*)

A. *Sample from an unaged normal roving bobbin, clamped at both ends to prevent dimensional change.*
B. *Sample from an unaged normal roving bobbin, after 5 days at 65% R.H., 70° F.*
C. *Sample* B, *after 9 additional hrs. at 95%–100% R.H.*
D. *Sample from an unaged normal roving bobbin, treated in oven at 239°F for 30 min. and then clamped at both ends.*
E. *Sample from an unaged normal roving bobbin, suspended in saturated steam for 2 min. and then clamped at both ends.*
F. *Sample from an unaged steamed roving bobbin, clamped at both ends.*
G. *Sample from an unaged steamed roving bobbin, after 5 days at 65% R.H., 70°F.*
H. *Sample from an unaged steamed roving bobbin, suspended in saturated steam for 5 min. and then clamped at both ends.*

*Dimensional Stability Experiments with Roving*

Further experiments on the dimensional changes due to crimp recovery were performed with roving. The results, some of which are illustrated in Figure 5, were very similar to those obtained with top. The samples shown in Figure 5 were not all originally the same length; therefore, this figure will be used to illustrate only changes of width.

*Dimensional changes due to crimp recovery.*—A sample of roving approximately 30 in. in length, removed from an unaged normal roving bobbin, and placed on a horizontal surface in an atmosphere at 65% R.H. and 70°F, free of the constraints of being wound on the bobbin, increased in width and decreased in length (compare the widths of samples *B* and *A* in Figure 5). Sample *A* shown in Figure 5 was clamped to the surface at both ends to prevent any further dimensional changes after it was removed from the bobbin. The steaming treatment of unaged roving appears to decrease the extent to which it expands after removal from the bobbin (compare samples *G* and *F* with *B* and *A* of Figure 5). Other experiments indicate that the same effect may be obtained through room-temperature aging for a much longer period.

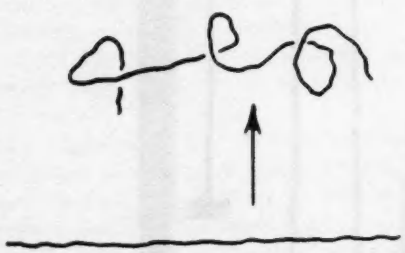

FIG. 6. *Change in crimp configuration when a single fiber extracted from top or roving is suspended in steam.*

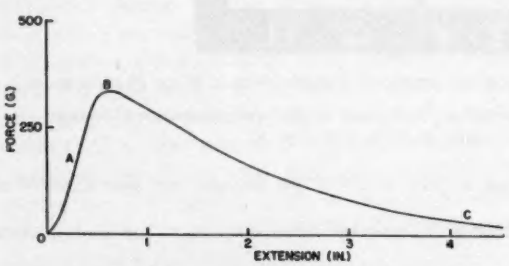


FIG. 7. *Typical force-extension curve for top. Rate of extension = 5 in./min., gage length = 10 in., 65% R.H., 70°F.*

*Effect of temperature and relative humidity on the dimensional changes due to crimp recovery.*—An increase in the temperature or relative humidity caused an increase in the rate and extent of the dimensional changes of normal roving strands freed of winding constraints (compare samples *C*, *D*, and *E* with *A*). The dimensional changes of unaged steamed roving were also increased by exposing the unconstrained roving strand to a high temperature and humidity (compare *H* with *F*), but the effects were not as pronounced as those observed with unaged normal roving.

*Crimp changes of the single fibers.*—Microscope inspection of the fibers in roving strands which exhibited dimensional changes showed that the crimp configuration of the fibers had changed. This tendency for fibers from top or roving to show crimp recovery can be demonstrated by removing a fiber from the assembly and suspending it for a few seconds in an atmosphere of steam. A schematic diagram of a fiber before and after such a treatment is presented in Figure 6.

*Measurement of Mechanical Properties*

During the extension of a strand of top or roving, gripped at ends much farther apart than the fiber staple length, fiber slippage rather than fiber breakage occurs as the strand is pulled apart. A typical force-extension curve for top is given in Figure 7, a typical curve for roving in Figure 8. A complete discussion of the measurement and interpretation of these force-extension curves is given in the third paper in this series [3]. In the region *OA* the extension of the strand takes place primarily through deformation of the fiber crimp; little fiber slippage occurs. At the

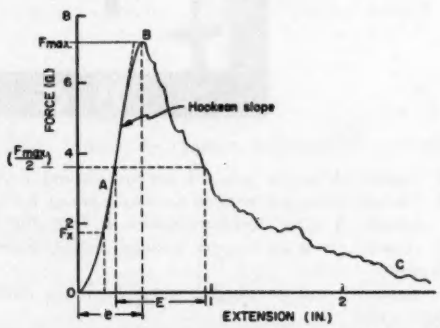


FIG. 8. *Typical force-extension curve for roving. Rate of extension = 5 in./min., gage length = 15 in., 65% R.H., 70°F.*

point of maximum load, *B*, however, the strand extension takes place mainly through fiber slippage. Further extension in the region *BC* results in fiber slippage in a localized section of the test length. As the number and length of fibers extending from one side of the break into the other decrease, the force necessary to maintain the constant rate of extension also decreases. Parameters used to describe these force-extension curves include the maximum load; the Hookean slope, defined as the steepest rate of increase of force in the region *OB* of the curve; and the energy to break, measured as the area under the force-extension curve.

### *Experiments on Mechanical Properties of Top*

*Normal top.*—The normal top balls used to supply samples for this study were aged in a conditioned room maintained at 65% R.H. and 70°F. At various times after processing samples of top were removed from the balls and were used to obtain force-extension curves descriptive of the mechanical behavior of the top at the time of measurement. The interval between the removal of the sample from the ball and the start of its extension in the tensile tester was less than 1 min.

TABLE III. COMPARISON OF THE MECHANICAL PROPERTIES OF SAMPLES FROM NORMAL AND STEAMED TOP BALLS (U. S. MEDIUM WOOL)

| | Maximum load (g.) | Hookean slope $\left(\frac{\text{g.}}{\text{cm./cm.}}\right)$ | Energy to break $\left(\frac{\text{g.-cm.}}{\text{cm.}}\right)$ |
|---|---|---|---|
| Normal top | 686 | 17,300 | 146 |
| Steamed top | 773 | 23,500 | 164 |

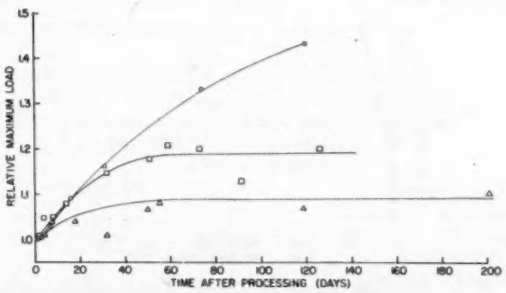


FIG. 9. *Changes of maximum load of normal top with aging time after processing.* ○—*U. S. fine wool;* △—*U. S. medium wool;* □—*New Zealand medium wool.*

Data presented in Figure 9 illustrate the change of maximum load with time of aging after processing. The maximum load, the Hookean slope, and the energy to break increased with aging time after processing.

*The effect of steaming the top balls.*—The steamed top balls were also allowed to age at 65% R.H. and 70°F. Here, too, samples were removed from the balls at various times after processing, and force-extension curves were obtained. A comparison of the mechanical properties for samples which were removed from normal and steamed top balls and

TABLE IV. THE EFFECT OF AGING ON THE MAXIMUM LOAD OF SAMPLES FROM STEAMED TOP BALLS (U. S. MEDIUM WOOL)

| Days after processing | Maximum load (g.) * Strand *1* | Strand *2* |
|---|---|---|
| 1 | 716 | 787 |
| 2 | 756 | 791 |
| 4 | 853 | 741 |
| 8 | 967 | 748 |
| 14 | 820 | 715 |
| 32 | 715 | 823 |
| 50 | 764 | 796 |
| 55 | 740 | 836 |
| 119 | 707 | 772 |
| 224 | 695 | 837 |

* Each value is the mean of 5 replications taken at nearby stations on the strand. The standard deviation of replications = 60.1 g.

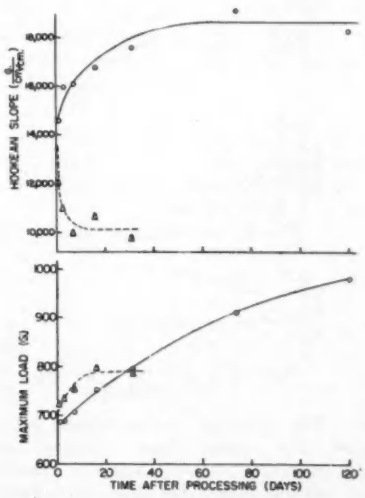


FIG. 10. *Comparison of normal aging and the effect of freeing the top strand from winding constraints. (Top made from the U. S. fine wool.)* ○—*Normal aging;* △—*Free of winding constraints.*

tested 2 days after processing is given in Table III. Samples from unaged steamed top balls had higher maximum loads, Hookean slopes, and energies to break than samples from unaged normal top balls. The mechanical properties of the steamed tops were not significantly affected by aging; however, the experimental error was much greater than that observed for the normal tops, and this may mask the changes. Typical results for the maximum load are given in Table IV. There is a highly significant strand-by-day interaction probably due to variation along an individual strand.

*The effect of freeing the top strand from winding constraints. Samples from unaged normal balls only.*—Shortly after processing, a large number of 20-inch lengths of top were removed from the normal top balls and were placed on a horizontal surface under atmospheric conditions of 65% R.H. and 70°F. These samples, free of the winding constraints impressed on the wool within a top ball, were extended to break at various times after removal from the ball to obtain data on the change in mechanical properties with time. The maximum load was found to increase and the Hookean slope to decrease with time after removal from the ball.

A comparison of the results for normal aging where the top was kept wound in the balls and the results of this experiment where the top was allowed to remain free of winding constraints is given in Figure 10. The samples which were allowed to remain free of winding constraints were removed from the balls about 8 hrs. after processing.

*The effect of freeing the top strand from winding constraints.*—The experiment described in the preceding section was extended to aged normal top and to unaged steamed top. In one typical experiment large numbers of samples were removed from a normal top ball about 12 hrs. after processing, at 91 days after processing, and at 225 days after processing. A large number of samples was also removed from a steamed top ball, also about 12 hrs. after processing. The results of measurements of mechanical properties are summarized in Figure 11 and indicate that the effect of freeing the top from winding constraints was different for samples from unaged normal and aged normal top balls. Also it was found that the mechanical behavior of the samples from the unaged steamed top balls appeared to simulate that of the samples from well-aged normal top balls.

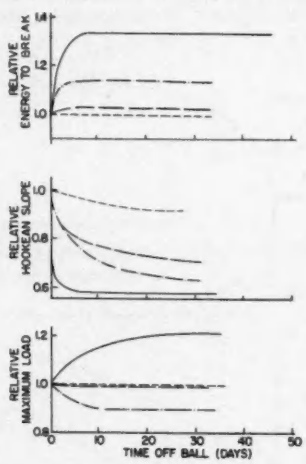


FIG. 11. *The effect on the mechanical properties of freeing the top strand from winding constraints (smoothed curves).* ———, *Samples removed from normal top ball less than 1 day after processing;* —·—·, *Samples removed from normal top ball 91 days after processing;* — — —, *Samples removed from normal top ball 225 days after processing;* - - - - -, *Samples removed from steamed top ball less than 1 day after processing.*

### *Experiments on Mechanical Properties of Roving*

*Normal roving.*—The normal roving bobbins were aged in a conditioned room maintained at 65% R.H. and 70°F. At various times after processing, sam-

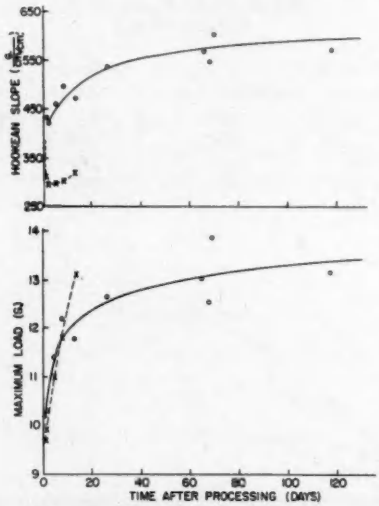


FIG. 12. *Comparison of normal aging and the effect of freeing the roving strand from winding constraints. (Roving made from the U. S. fine wool.)* ○—*Normal aging;* ×—*Free of winding constraints.*

ples of roving were removed from the bobbins and force-extension curves were obtained. The interval between the removal of the sample from the bobbin and the start of extension in the tensile tester was less than 1 min. The results of a typical series of measurements are presented in Figure 12. The maximum load, Hookean slope, and energy to break were found to increase with aging time after processing. These results are quite similar to those obtained with top.

*The effect of steaming the roving bobbin.*—The steamed roving bobbins were also allowed to age at 65% R.H. and 70°F. Samples were also removed from the bobbins at various times after processing and force-extension curves were obtained. A comparison of the mechanical properties for samples which were removed from normal and steamed roving bobbins and tested 24 hrs. after processing is given in Table V. Samples from unaged steamed roving bobbins had higher values for maximum load, Hookean slope, and energy to break than samples from unaged normal roving bobbins. Again the results were similar to those obtained with top. However, for samples taken off the steamed roving bobbins and tested at various times after processing, there was evidence that the maximum load, the Hookean slope, and the energy to break increased with aging time after processing. Some results obtained on the mechanical properties of steamed roving made from the U. S. medium wool are presented in Table VI.

*The effect of freeing the roving strand from winding constraints.*—In an experiment with the roving made from the U. S. fine wool, large numbers of 30-inch lengths of roving were removed from a normal roving bobbin about 10 hrs. after processing and were allowed to hang vertically under atmospheric conditions of 65% R.H. and 70°F. As in the similar experiment with top, these samples—free of the winding contraints impressed on the wool within a roving bobbin—were tested at various times to obtain the force-extension curves. The dashed curves of Figure 12 present typical results. Comparison of the solid and dashed curves shows that the change of mechanical properties of roving aged on the bobbin differs from that of the roving allowed to remain free of winding constraints.

A similar experiment was performed on roving made from the New Zealand medium wool. Samples were removed from bobbins of normal roving 17 hrs. after processing and again at 90 days after processing and from a bobbin of steamed roving at 17 hrs. after processing. The results of measurements of mechanical properties are summarized in Figure 13 and indicate that, as with top, the behavior of unaged steamed roving is more nearly equivalent to that of aged rather than unaged normal roving.

*Regain changes during the aging period.*—If the top balls or roving bobbins are not at a uniform moisture regain, or if their moisture regain is not in equilibrium with the atmosphere under which they are aging, changes in regain will take place during aging in the mill. In the present work no measurements were made until the samples had been in the conditioned room for at least 12 hrs. Furthermore, all samples were taken from the outer layers of the balls or bobbins. Experiments with roving bobbins showed that for the possible range of differences between the mill processing conditions and those in the conditioned room (65% R.H., 70°F) this was sufficient pre-conditioning. Therefore, the results obtained in the present work are not due to changes in moisture regain of the wool.

TABLE V. COMPARISON OF THE MECHANICAL PROPERTIES OF SAMPLES FROM NORMAL AND STEAMED ROVING BOBBINS (U. S. MEDIUM WOOL)

| | Maximum load (g.) | Hookean slope $\left(\frac{\text{g.}}{\text{cm./cm.}}\right)$ | Energy to break $\left(\frac{\text{g.-cm.}}{\text{cm.}}\right)$ |
|---|---|---|---|
| Normal roving | 10.5 | 456 | 0.63 |
| Steamed roving | 18.5 | 831 | 0.85 |

TABLE VI. THE EFFECT OF AGING ON THE MAXIMUM LOAD OF SAMPLES FROM STEAMED ROVING BOBBINS (U. S. MEDIUM WOOL)

| Days after processing | Maximum load (g.) * Strand *1* | Strand *2* |
|---|---|---|
| 1 | 17.6 | 19.4 |
| 4 | 17.9 | 18.7 |
| 8 | 20.9 | 19.5 |
| 13 | 19.1 | 20.6 |
| 18 | 21.7 | 19.9 |
| 26 | 23.0 | 21.8 |
| 33 | 22.7 | 20.6 |
| 41 | 20.8 | 22.1 |
| 53 | 23.7 | 21.6 |
| 109 | 21.3 | 21.6 |

* Each value is the mean of 5 replications taken at nearby stations on the strand. The standard deviation of replicatons = 2.64 g.

## Discussion of Experimental Results

The fibers in the top balls or roving bobbins have been deformed in two ways, each of which affects primarily the crimp in the fibers:

*Removal of crimp.*—During the carding, gilling, combing, and drawing operations the fibers are subjected to tensions which cause deformation (removal) of the crimp present in the scoured wool.

*Winding deformation.*—Strands of top or roving wound onto the ball or bobbin are laterally compressed. This increases the packing density of the fibers in the assembly and causes slight lateral deformations of the crimps.

The constraints impressed on the wool within the ball or bobbin prevent motion of the fibers, but when the strand of top or roving is removed from the ball or bobbin, and is thus freed of winding constraints, the fibers can exhibit recovery from the above deformations. Since the crimp-removal deformations probably exceed the yield point of the fibers to a greater degree than do the winding deformations, the bulk of the crimp recovery should be slower than the unwinding recovery.

During normal aging the fibers are maintained in the deformed state allowing relaxation of the internal stresses which cause the recoveries. The fibers are temporarily set into the deformed state, and the tendency to exhibit recovery is reduced.

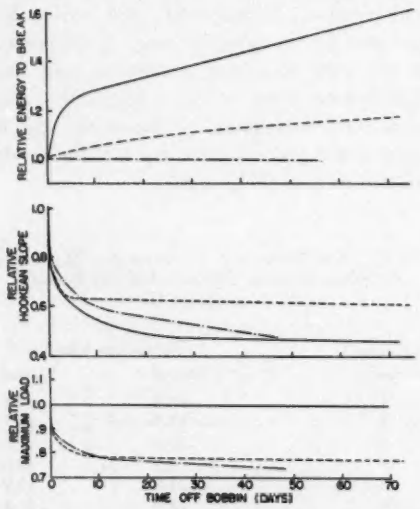


FIG. 13. *The effect on the mechanical properties of freeing the roving strand from winding constraints (smoothed curves).* ———, *Samples removed from normal roving bobbin less than 1 day after processing;* —·—·, *Samples removed from normal roving bobbin 90 days after processing;* — — —, *Samples removed from steamed roving bobbin less than 1 day after processing.*

The dimensional instabilities of unaged normal top or roving are due to the recovery processes described above. Aging temporarily sets the fibers and inhibits the dimensional changes. The effect on the dimensional changes of increasing the temperature or humidity to which unconstrained normal top or roving is exposed is consistent with the well-known effect of these parameters on the tensile recovery behavior of single wool fibers.

During the process of removing a sample of top or roving from the ball or bobbin and placing it in the jaws of the tensile tester, unwinding recovery can occur. This unwinding recovery will take place to a greater extent with samples from unaged normal top balls or roving bobbins than with samples from aged normal balls or bobbins. The decrease of the density of packing of fibers in the assembly incident on the unwinding recovery causes the maximum load, the Hookean slope, and the energy to break to decrease [3]. Therefore, the measured values of these parameters are greater for samples taken from aged normal top balls or roving bobbins than for samples from unaged normal balls or bobbins.

Consider now the experiment where the mechanical properties were measured as a function of time after freeing the samples from winding constraints. The zero points in Figures 11 and 13 correspond to a time off the ball or bobbin of less than 1 min. For samples removed from the normal ball or bobbin a short time after processing, most of the unwinding recovery has occurred before this zero point measurement, and further change is due to the slower crimp recovery. This crimp recovery causes the Hookean slope to decrease [3] and has a complex effect on the maximum load. (The crimp recovery influences the maximum load both by increasing the degree of fiber interlocking and by decreasing the density of fiber packing.) Note the differences in the change of mechanical properties for this experiment (crimp recovery) and for the experiment where samples were tested shortly after removing from the normal ball or bobbin (diminution of unwinding recovery).

Aging the normal top balls or roving bobbins before freeing the samples of top or roving inhibits the unwinding recovery to a degree that permits it to

be measured; the crimp recovery is even more strongly inhibited. Thus the difference between the change of mechanical properties for samples freed shortly after processing and after an aging period arises from the former being due largely to crimp recovery and the latter being due largely to unwinding recovery.

It is well known that stress relaxation in wool fibers can be accelerated by heat and moisture. Thus, by steaming the top balls or roving bobbins, it should be possible to shorten the time needed to set the fibers temporarily in the deformed state. Indeed a short steaming of the unaged top balls or roving bobbins did have many of the same effects on the properties of these assemblies as a long aging time at 65% R.H. and 70°F: the dimensional changes due to unwinding and crimp recovery were inhibited; the maximum load, the Hookean slope, and the energy to break were increased; and the changes of mechanical properties on freeing the strands from winding constraints were more equivalent to those for samples from well-aged normal top balls or roving bobbins than to those from unaged normal balls or bobbins. However, there was some evidence that the steamed roving did show a change of mechanical properties with normal aging; this is discussed below.

Although aging or a mild steaming of the normal top balls or roving bobbins does inhibit the recovery processes, the fibers are not permanently set. For example, a strand of roving aged on the bobbin at 65% R.H. and 70°F will show little dimensional change when freed in an atmosphere of the same conditions. If, however, it is freed in an atmosphere in which either the temperature or the humidity has been increased, it will undergo dimensional changes.

Several investigators [2, 5, 6, 10] have shown that the oils added during processing can undergo oxidation during aging. The tops used in these experiments had no added oil, and, unless processing has affected its chemical composition, it is doubtful that the residual wool grease undergoes any changes during the aging period. The rovings, however, contained a small amount of peanut oil, and oxidation of this oil with the resultant setting up of adhesions between the fibers might have contributed to the changes observed during the aging of the rovings. Thus there was evidence that samples removed from steamed roving bobbins during the aging period showed a progression of mechanical properties, whereas there was no such evidence for samples from the steamed top balls.

The tops and rovings studied in this work had no net twist. The aging of twisted (Bradford) rovings may be concerned with deformations due to the twist as well as with the crimp deformations discussed above. Future work on the Wool Research Project will also be concerned with the aging of twisted rovings.

## Summary

Measurements of the changes in the physical properties of top and roving have been made throughout aging times up to several hundred days at 65% R.H. and 70°F. The effects of two aging conditions have been studied: (*1*) aging of top and roving constrained by being wound on the ball or bobbin, and (*2*) removing these assemblies from the ball or bobbin and allowing them to remain free of constraint.

Sample strands of top and roving expand laterally when the winding constraints are removed directly after processing. Samples removed after aging at 65% R.H. and 70°F for several months, or after a mild steaming treatment, show a decreased rate and extent of lateral expansion. The level of such mechanical properties as the Hookean slope, maximum load, and energy to break increases during aging.

The change in mechanical properties of free or unconstrained top and roving differs from that measured on samples aged under constraint and depends upon their previous history of constrained aging.

These experimental results indicate that one consequence of aging is a relaxation of stresses in the fiber caused by deformations of the fiber crimp during previous processing. The deformations are of two kinds—removal of crimp during the carding, gilling, combing, and drawing operations, and lateral deformation of the crimp caused by winding the strands of top or roving onto the ball or bobbin. The stress relaxation causes the fibers to be temporarily set into the deformed state. This relaxation process is accelerated by heat or moisture, and a short steaming of the fresh top balls or roving bobbins has many of the same effects on the properties of these assemblies as does a long aging time at 65% R.H. and 70°F.

## Acknowledgment

The author wishes to thank Dr. T. F. Evans, Mrs. C. Piper, Mrs. C. Price, and Mr. W. O. Seifert for

their assistance in various phases of this work. The data in Table I were obtained by Mr. H. Wolf of the Forstmann Woolen Company. Dr. J. H. Wakelin, under whose direction this work was done, Prof. J. C. Whitwell, and Prof. R. K. Toner contributed many valuable ideas and criticisms.

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# Properties of Apparel Wools

## VII. The Mechanical Behavior of Roving*

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THE measurement and interpretation of the tensile force-extension curves for rovings produced on the French worsted system were discussed in a preceding paper in this series [1]. The present paper describes two applications of these measurements in the comparison of rovings made from different wools.

### Comparison Between Four Apparel Wools

The Wool Research Project was concerned with an evaluation of the properties and processing of four wools: an Australian 70's grade Merino, a New Zealand 58's grade crossbred, a U. S. 64's grade Rambouillet, and a U. S. 58's grade crossbred. These wools were processed into roving at separate times, often on different units of the same type of drawing equipment. A summary of these processing operations was given in the first paper in this series [3]. Some characteristics of the rovings produced during the main processing trials are given in Table I.

TABLE I. CHARACTERISTICS OF THE ROVINGS PRODUCED DURING THE MAIN PROCESSING TRIALS

| | Weight per unit length (g./m.) | Fiber fineness (μ) | Fiber length (in.) | Moisture content (%) | Ether extractable matter (%) |
|---|---|---|---|---|---|
| Australian fine | 0.214 | 19.8 | 2.46 | 14.2 | 0.40 |
| U. S. fine | 0.215 | 21.6 | 2.88 | 14.6 | 0.82 |
| U. S. medium | 0.212 | 26.2 | 3.35 | 13.4 | 0.84 |
| New Zealand medium | 0.220 | 26.1 | 3.33 | 13.2 | 1.24 |

*This work was conducted as part of the Wool Research Project sponsored by the American Wool Council; the International Wool Secretariat; the National Wool Trade Association; the Office of Naval Research, Department of the Navy; and by a number of American wool manufacturing firms. Other phases of the project are sponsored by the Agricultural Research Service, U. S. Department of Agriculture (RMA Contract A-1s-30934).

Parts I-V appeared in the Feb., 1952, July, 1952, July, 1953, Oct., 1953, July, 1954, issues, respectively. Part VI appears in this issue, p. 716.

†At present on active duty in the United States Air Force.

About 2 years after the main processing trials a series of samples for a comparison between the wools was prepared in the following manner. For each wool, four strands (from two double-meche bobbins) of the roving produced during the main processing trials were processed through a porcupine drawing head on the roving finisher. A draft of 2.44 was used, and one double-meche bobbin of the redrawn sample was produced. The four wools were processed simultaneously on four different drawing heads. The wool-drawing head relationships were then changed until a small amount of the redrawn sample had been produced from each wool using each of the four drawing heads. A total of sixteen double-meche bobbins, four from each wool, were obtained.

Force-extension curves were measured for two adjacent samples from each strand of roving. A typical force-extension curve is given in Figure 1. The averages of the two values of Hookean slope or maximum load measured on each strand are given in Table II. Note the pronounced differences among strands produced on different machine units [1].

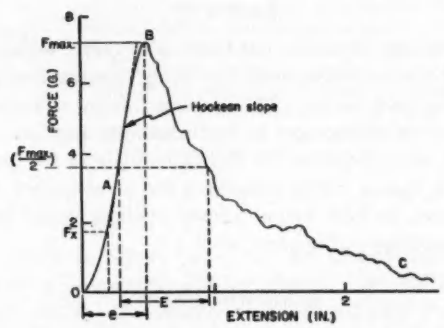


FIG. 1. *A typical force-extension curve for roving. Rate of extension = 5 in./min., gage length = 15 in., 65% R.H., 70°F.*

For a given type of wool, the maximum load has a complicated dependence on fiber length, diameter, modulus of elasticity, interfiber coefficient of friction (and therefore on oil and residual grease content), and crimp. Since most of these properties differ among the wools, it is not attempted, at this time, to interpret the differences in maximum load among the wools. However, the early region *OA* of the force-extension curve depends primarily on the fiber crimp and on the fiber modulus of elasticity. Since the fiber modulus of elasticity does not differ greatly among the wools [2], differences among the wools in the region *OA* of the force-textension curve should reflect differences in the fiber crimp. The higher the fiber crimp, the smaller should be the rate of increase of force in this region of the curve.

It has been pointed out [1] that the Hookean slope depends both upon the rate at which the force increases in the early region of the force-extension curve and upon the maximum load. The dependence of Hookean slope on maximum load can be obtained from a plot of the strand means given in Table II, and comparison of the Hookean slopes at comparable maximum loads leaves only the effect of the early region of the force-extension curve. Such a plot, on logarithmic coordinates, is given in Figure 2. It is evident that the Australian fine wool differed from the other wools; the lower Hookean slope at comparable maximum loads was due to a slower rate of increase of force in the region *OA* of the force-extension curve, and indicates that the fibers in the rov-

TABLE II. PHYSICAL PROPERTIES OF THE REDRAWN ROVING SAMPLES.* HOOKEAN SLOPE: $\left(\frac{\text{G.}}{\text{CM./CM.}}\right)$ = H.S., MAXIMUM LOAD: (G.) = M.L.

| Head | 1 | | | | 2 | | | | 3 | | | | 4 | | | | Averages | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| meche | L | | R | | L | | R | | L | | R | | L | | R | | Hookean | Maximum |
| property | H.S. | M.L. | H.S. | M.L. | H.S. | M.L. | H.S. | M.L. | H.S. | M.L. | H.S. | M.L. | H.S. | M.L. | H.S. | M.L. | slope | load |
| Australian fine | 416 | 11.0 | 481 | 13.4 | 567 | 16.8 | 502 | 14.1 | 443 | 11.8 | 585 | 15.4 | 554 | 14.4 | 315 | 8.6 | 483 | 13.2 |
| New Zealand medium | 638 | 13.6 | 427 | 9.0 | 835 | 19.0 | 603 | 13.5 | 597 | 13.1 | 787 | 17.2 | 708 | 16.1 | 463 | 10.2 | 632 | 14.0 |
| U. S. fine | 647 | 16.0 | 762 | 17.5 | 885 | 21.2 | 621 | 14.0 | 653 | 14.7 | 977 | 21.8 | 753 | 15.6 | 484 | 9.9 | 723 | 16.3 |
| U. S. medium | 767 | 17.3 | 513 | 10.9 | 668 | 15.0 | 535 | 12.3 | 627 | 13.1 | 1090 | 23.8 | 890 | 19.8 | 420 | 10.3 | 689 | 15.3 |
| Averages | 617 | 14.5 | 546 | 12.7 | 739 | 18.0 | 565 | 13.5 | 580 | 13.2 | 860 | 19.6 | 726 | 16.5 | 420 | 9.8 | | |

* Standard deviation of replications from a single strand: Maximum load, 1.66 g., Hookean slope, 64.2 $\left(\frac{\text{g.}}{\text{cm./cm.}}\right)$.

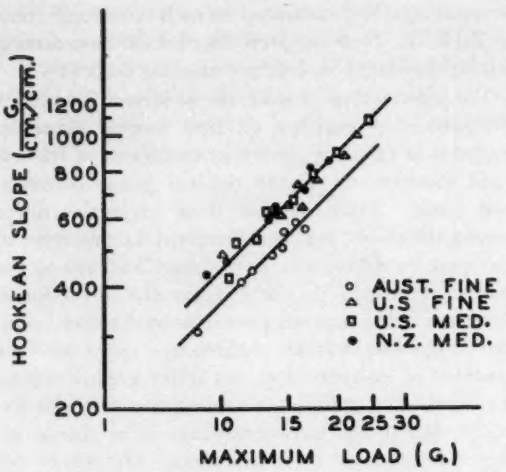


FIG. 2. *Plots of Hookean slope* vs. *maximum load of rovings made from the four apparel wools.*

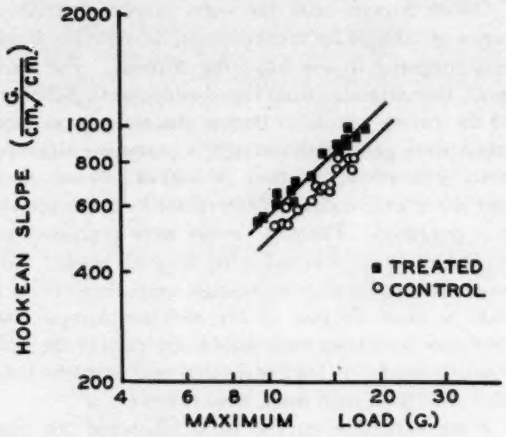


FIG. 3. *Plots of Hookean slope* vs. *maximum load of rovings made from untreated wool and from mechanically crimped wool.*

ing made from this wool had more crimp than the fibers in the rovings made from the other wools.

### The Effect of Processing on Mechanically Introduced Crimp

In another series of experiments a study was made of the effect on subsequent processing of adding a mechanically introduced crimp to the sliver after carding and one gilling operation. In this small-scale mill trial a control lot and the treated lot were processed in series on the same equipment. The force-extension curves of samples of the rovings produced were measured in a manner similar to that described above. Figure 3 shows plots of Hookean slope *vs.* maximum load. The rate of increase of force in the early regions of the force-extension curve was found to be greater for the roving made from the treated lot, indicating that the fibers in this roving had a lower crimp level. It would appear that the mechanical crimping process destroyed some of the natural crimp, but that the mechanically introduced crimp was less stable than was the normal crimp to the mechanical working that the fibers encountered during worsted processing.


### Summary

The rate of increase of force in the early region of the force-extension curve for roving depends strongly on the fiber crimp. The Hookean slope, when corrected for differences in the maximum load, can be used to characterize this rate of increase of the force, and is thus a useful parameter for investigating differences in fiber crimp among rovings made from various types of apparel wool.



### Acknowledgment

The author wishes to acknowledge the assistance of Mrs. Luba Ross and Mrs. Carol Piper in the measurements of the force-extension curves of the rovings. Much of the data in Table I was supplied by Mr. Harold W. Wolf of the Forstmann Woolen Co.


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# The Relationship of the Geometry of Plain Knit Cotton Fabric to Its Dimensional Change and Elastic Properties

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**Abstract**

A study was made of the geometry of 34 different plain knit cotton fabrics which were knit, in a wide range of stiffness, of six different yarns (12/1, 20/1, 28/1, 36/1, 40/1, 50/1). Stitch length in terms of course and wale spacings and diameter of yarn ranged from $l = 2p + w + 4.34d$ to $l = 2p + w + 6.37d$, as compared with the theoretical value of $l = 2p + w + 5.94d$ which Peirce derived.

Both the gray and the finished fabrics exhibited distortion. Laundering with screen- or tumbler-drying brought about rearrangement in the structure so that the data for wale and course spacings of the laundered fabrics followed the parabolic curve $p^2 = a\ (w + b)$. When fabrics were given a relaxation treatment to remove distortion, the data of wale and course spacings both before and after laundering also followed a parabolic curve. For the relaxed fabrics, dimensional changes in length and width in laundering were not excessive and did not vary with cover factor (stitch length/diameter of yarn).

The elastic properties changed greatly with cover factor for the unlaundered, relaxed, and laundered fabrics. As cover factor increased, the strain increased linearly when the fabrics were not distorted. Cover factor varied linearly with recovery and permanent set, with delayed recovery and permanent set increasing and immediate elastic recovery decreasing. Poisson's ratio increased somewhat with cover factor when the fabrics were not distorted.

IN previous papers [2, 3, 4] the present authors discussed the geometry of knit goods, reporting data which verified the theoretical equations that Peirce derived for weight and stitch length in terms of diameter of yarn and wale and course spacings [5]. Also investigated were the changes that occur in the fabric geometry in laundering. Included in the earlier studies were six plain knit materials of 30/1 yarn knit on one machine. The research reported herein includes 34 fabrics made from cotton yarns varying from fine to coarse and knit on different cuts of machines. The study reveals the effect of the geometry of fabrics on their stress-strain properties as well as on dimensional changes in laundering.

## Materials

The 34 fabrics * studied were plain knit and were made of six different cotton yarns (12/1, 20/1, 36/1, 40/1, 50/1). The yarns were medium-staple combed Peeler of Z twist (Table I).

* Fabrics were knit under controlled conditions in the Textile Research Department of the American Viscose Corp.

A 16-cut circular machine of 20 in. diameter was used for knitting the 12/1 and 20/1 yarns; a 28-cut machine of 22 in. diameter for the 28/1 and 36/1 yarns; and a 34-cut machine of 22 in. diameter for the 40/1 and 50/1 yarns.

Fabrics of four to seven different courses per inch were knit of each yarn (Table II). Some of the yardage of the gray goods was set aside, and the remainder was scoured and bleached.

TABLE I. NUMBER, TWIST, AND DIAMETER OF YARNS

| Yarn | Number (Cotton system) | Twist (direction and turns/in.) | Diameter (0.001 in.) |
|---|---|---|---|
| 12/1 | 11.74 | Z 9.4 | 14.53 |
| 20/1 | 20.58 | Z 12.3 | 10.98 |
| 28/1 | 27.64 | Z 15.4 | 8.859 |
| 36/1 | 35.88 | Z 21.0 | 7.094 |
| 40/1 | 39.34 | Z 19.4 | 6.467 |
| 50/1 | 51.08 | Z 23.2 | 5.509 |

### Method

The diameter of the yarns, stitch length, and wale and course counts were determined as described previously [2].

As before, the cotton knit goods were laundered at 212°–140°F. In screen-drying, each specimen after the last rinse was floated in water over a wire screen placed on the bottom of a tray. Both fabric and screen were lifted from the tray, and the material was not removed from the screen until dry. In tumbler-drying, the specimens were extracted for 3 min. and then tumbled for 40 min. at 143°–163°F.

TABLE II. WALE AND COURSE COUNT, WEIGHT, AND STITCH LENGTH OF KNIT FABRICS

| Fabrics | Gray Courses/ in.* | Finished Wales/ in. | Finished Courses/ in. | Finished Weight (oz./ sq. yd.) | Finished Stitch length (0.001 in.) |
|---|---|---|---|---|---|
| Knit of 12/1 | | | | | |
| 1 | 18 | 21.5 | 18.6 | 4.98 | 223.0 |
| 2 | 22 | 22.5 | 20.6 | 5.18 | 204.2 |
| 3 | 26 | 23.3 | 23.9 | 5.74 | 190.4 |
| 4 | 30 | 23.4 | 28.4 | 6.26 | 169.9 |
| Knit of 20/1 | | | | | |
| 5 | 18 | 24.7 | 17.7 | 3.02 | 211.2 |
| 6 | 22 | 24.3 | 20.6 | 3.06 | 195.6 |
| 7 | 26 | 26.4 | 23.6 | 3.64 | 176.0 |
| 8 | 30 | 28.1 | 27.9 | 3.56 | 157.5 |
| 9 | 34 | 29.1 | 29.2 | 3.90 | 150.8 |
| Knit of 28/1 | | | | | |
| 10 | 22 | 33.8 | 22.8 | 3.00 | 160.0 |
| 11 | 26 | 34.4 | 25.2 | 2.98 | 153.1 |
| 12 | 30 | 36.2 | 30.2 | 3.48 | 137.8 |
| 13 | 34 | 36.1 | 34.9 | 3.76 | 124.7 |
| 14 | 38 | 38.2 | 37.9 | 3.82 | 122.1 |
| 15 | 42 | 39.4 | 41.5 | 4.06 | 114.1 |
| Knit of 36/1 | | | | | |
| 16 | 22 | 35.7 | 22.7 | 2.60 | 164.2 |
| 17 | 26 | 37.8 | 25.4 | 2.78 | 148.7 |
| 18 | 30 | 37.4 | 30.2 | 2.80 | 135.8 |
| 19 | 34 | 37.5 | 33.1 | 3.10 | 129.6 |
| 20 | 42 | 38.0 | 35.3 | 3.08 | 121.4 |
| 21 | 46 | 37.7 | 40.5 | 3.38 | 109.9 |
| Knit of 40/1 | | | | | |
| 22 | 26 | 38.7 | 27.9 | 2.64 | 138.2 |
| 23 | 30 | 41.0 | 32.9 | 3.08 | 121.0 |
| 24 | 34 | 41.1 | 34.3 | 3.12 | 118.3 |
| 25 | 38 | 42.5 | 37.9 | 3.22 | 112.6 |
| 26 | 42 | 42.3 | 43.0 | 3.50 | 103.5 |
| 27 | 46 | 43.4 | 45.9 | 3.54 | 99.6 |
| Knit of 50/1 | | | | | |
| 28 | 26 | 43.0 | 27.9 | 2.34 | 135.8 |
| 29 | 30 | 41.8 | 32.6 | 2.46 | 126.4 |
| 30 | 34 | 41.3 | 35.6 | 2.56 | 116.0 |
| 31 | 38 | 43.5 | 38.2 | 2.76 | 108.0 |
| 32 | 42 | 45.4 | 42.0 | 2.88 | 102.6 |
| 33 | 46 | 44.4 | 46.6 | 3.03 | 97.6 |
| 34 | 50 | 45.9 | 49.9 | 3.14 | 92.0 |

* Courses were counted with the fabric in a relaxed condition after removal from the knitting machine.

One set of three specimens, 15 in. square, was used to obtain data on dimensional changes in five launderings with screen-drying. A second set was laundered, extracted, and tumbler-dried five times.

Two additional sets of specimens were relaxed to reduce distortion and to bring wale and course spacings into relationships approximating those of the laundered fabric. One relaxation treatment was done by manual manipulation and the other by tumbler-drying.

The relaxation treatment by manual manipulation consisted of stretching or shrinking the cloth which had been soaked in warm water for 2 hrs. to approximately the dimensions assumed by a similar area of laundered fabric. The material was then floated over a screen and allowed to dry without tension. The relaxed specimens were marked, and then laundered and screen-dried five times.

The relaxation treatment by tumbler-drying consisted of soaking the specimens in warm water for 2 hrs., extracting, and then tumbler-drying for 40 min. at 143°–163°F. The relaxed specimens were marked, and then laundered and tumbler-dried five times.

The stress-strain properties were determined under standard conditions (65% relative humidity and and 70°F) by a procedure developed in the Bureau's laboratory [1]. Since plain knit goods exhibit only small strains when stresses are applied along the direction of the wales, results for this study are reported only for stresses applied crosswise or at right angles to the wales. For the measurements, six specimens were cut 12 in. by 8 in., with the shorter dimension parallel to the wales or lengthwise of the fabric.

The specimen was laid flat on a table with no stress applied. Three 5-in. lengths, 1 in. apart, were marked off in each direction. Then the specimen was placed on the pins of the machine so that a load could be applied at right angles to the wales. A 200-g. load was applied, and the three marked lengths in each direction were measured. As soon as the readings were recorded, the load was removed and the fabric was allowed to recover. A load of 30 g. was applied, which was just enough to straighten but not

to stretch the fabric. The 30-g. load was removed, and readings were again taken of the marked lengths in both directions. The procedure was repeated with loads at intervals from 200 to 2,000 g. Approximately 8 min. were required to take the readings for one specimen. After the last reading, the specimen was removed from the apparatus and laid flat on a table. Measurements were made of the marked lengths at the end of 1 hr.

The average elongations in inches for the six specimens with load and with load removed were plotted against load. From the graphs, calculations were made of the elongation, elastic recovery, and Poisson ratio at various loads. From the readings taken at the end of 1 hr., determination were made of delayed recovery and permanent set.

## Results and Discussion

### *Length of Stitch*

In the analysis of data, stitch length was first considered. The measured stitch lengths are given in Table II. The equation of stitch length derived by Peirce for flat plain knitting is

$$l = 2p + w + 6 \cdot \sqrt{4/\pi \cdot g/\rho},$$

which can also be expressed as

$$l = 2p + w + 5.94d,$$

where $l$ is the length of yarn in a unit cell or in one stitch, $p$ is the course spacing, $w$ is the wale spacing, $g$ is the weight per unit length of yarn, $\rho$ is the yarn density, and $d$ is the diameter of the yarn.

The following equations express the measured stitch length for fabrics knit of the six yarns:

12/1 yarn, $l = 2p + w + 4.34d$;
20/1 yarn, $l = 2p + w + 4.85d$;
28/1 yarn, $l = 2p + w + 4.79d$;
36/1 yarn, $l = 2p + w + 5.86d$;
40/1 yarn, $l = 2p + w + 5.54d$;
50/1 yarn, $l = 2p + w + 6.37d$.

The measured stitch lengths for fabrics knit of 36/1 and 40/1 yarns are in excellent agreement with those calculated from Peirce's theoretical equation. The measured values for stitch length are slightly

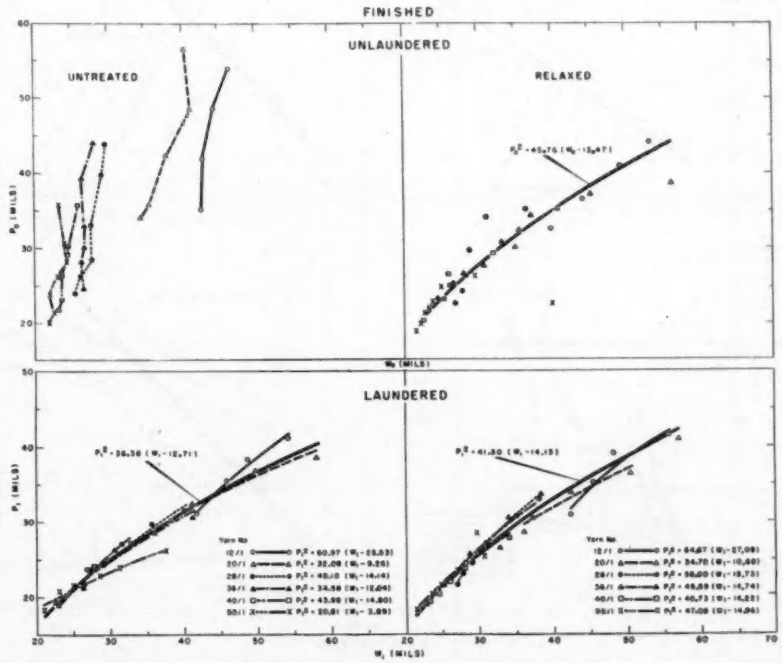


FIG. 1. *The relationship of wale spacings* (w) *to course spacings* (p) *before and after laundering of the finished and relaxed finished fabrics.* $w_0$ *and* $p_0$ *indicate spacings before laundering;* $w_1$ *and* $p_1$ *indicate spacings after laundering.*

lower for those knit of 12/1, 20/1, and 28/1 yarns, and slightly higher for those knit of 50/1 yarn.

*Effect of Geometry upon Dimensional Change*

*Laundering with screen-drying.*—Distortion was apparent in the curves for both the gray and the finished unlaundered fabrics, and the wale and course spacing relationship was not the same for all. Laundering brought about marked changes in the relationship of wale and course spacings of all the fabrics. After laundering, the wale spacings plotted against course spacings followed a parabolic curve, such as $p^2 = a\ (w + b)$. The relationship between $p$ and $w$ was the same for fabrics knit of fine as well as coarser yarns, as shown by the fact that the data for $p$ and $w$ of the gray and the finished laundered fabrics knit of each yarn approximated the same parabolic curve. The $p$ and $w$ curves for the finished fabrics are shown in Figure 1.

Distortion was also eliminated by the manual relaxation treatment. After this treatment, the wale and course spacings for fabrics knit of all the yarns followed a parabolic curve, and the equation for each was approximately the same as that for the curve of the same fabric after laundering. Therefore, the relaxation treatment was such that the relationship of wale and course spacings was the same before and after laundering.

The relationship of wale spacings before laundering, $w_0$, to wale spacings after laundering, $w_1$, of both the gray and finished fabrics indicates considerable distortion in the width of the fabrics. Figure 2 shows this relationship for the finished fabrics. Since the relationship of course spacings before to those after laundering approximates a straight line, the distortion in the length is not excessive, but both the gray and finished materials need to be stretched in the width to eliminate distortion.

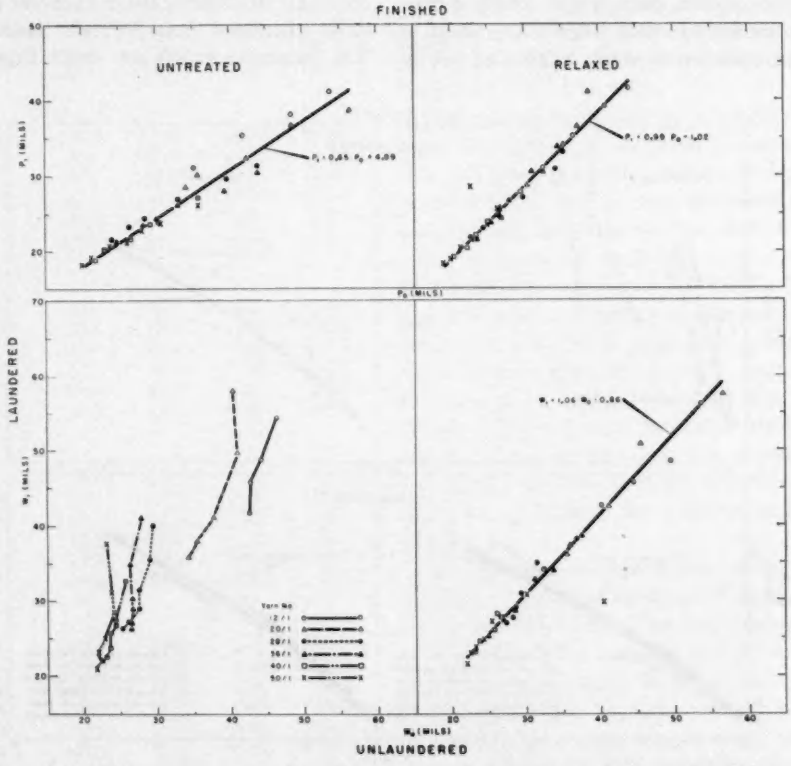


FIG. 2. *The relationship of course spacings* (p) *to wale spacings* (w) *before and after laundering of the finished and relaxed finished fabrics.* $w_0$ *and* $p_0$ *indicate spacings before laundering;* $w_1$ *and* $p_1$ *indicate spacings after laundering.*

After the relaxation treatment, these relationships were linear, and the changes in dimensions of the unit cell were similar for the fabrics knit of all the yarns.

Changes of dimensions in laundering were considerable for many of the finished fabrics (Figure 3). Shrinkage in length ranged from 11% to 30%. In width, dimensional change ranged from 3% shrinkage to 63% stretch. Those fabrics stretching the most were the loosely knit ones having the higher cover factor, stitch length/yarn diameter ($l/d$). Since the stretching in width compensated in large part for the shrinkage in length, the range for change in area was not as great—17% shrinkage to 1% stretch. There was only a slight trend towards a decrease in area shrinkage with an increase in cover factor.

For the relaxed fabrics, dimensional changes in length and width in laundering were never excessive and did not change with cover factor (Figure 4). The majority stretched less than 5% in width and shrank between 5% to 10% in length. Shrinkage in area ranged from 0% to 18%, and increased slightly with cover factor.

*Laundering with tumbler-drying.*—The equations expressing the relationship of wale and course spacings for the laundered fabrics are practically identical, whether screen-drying or tumbler-drying is used (Figures 1 and 5). However, the deviation from the parabolic curve of the fabrics relaxed by tumbler-drying (Figure 5) is greater than that of the fabrics relaxed by the manual relaxation treatment (Figure 1). Likewise, a comparison of Figure 4 with similar data for tumbler-dried fabrics reveals a more nearly linear relationship between wale spacings before and after laundering when the fabrics are relaxed manually than when relaxed by tumbler-drying.

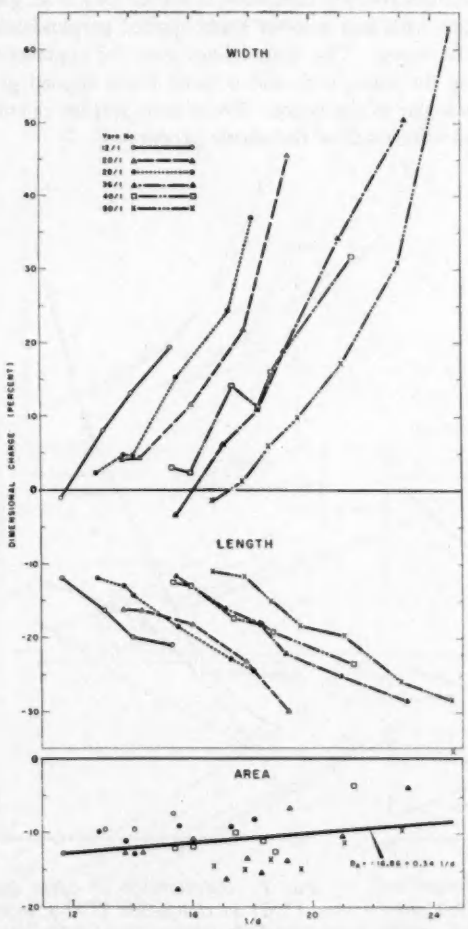


FIG. 3. *Relationship of cover factor* (l/d) *to dimensional change of width, length, and area* ($D_a$) *in 5 launderings of the finished fabrics.*

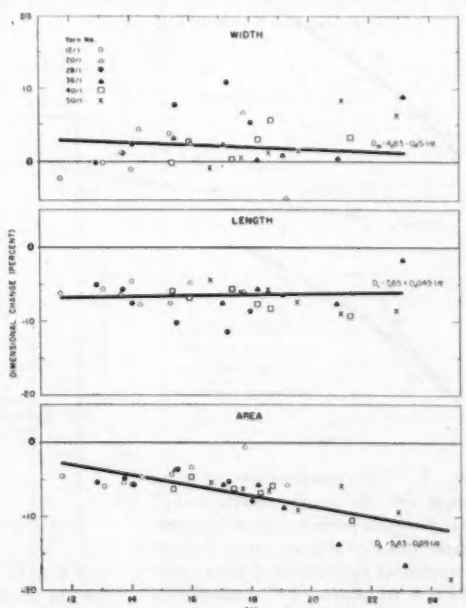


FIG. 4. *Relationship of cover factor* (l/d) *to dimensional change of width* ($D_w$), *length* ($D_l$), *and area* ($D_a$) *in 5 launderings of the finished relaxed fabrics.*

It is well known that laundering with tumbler-drying consolidates the loop construction of knit goods, and the dimensional change is different from that in laundering with screen-drying. Shrinkage in length with tumbler-drying ranged from 15% to 36% as compared to a range from 11% to 30% with screen-drying. In width, dimensional change ranged from 6% shrinkage to 44% stretch with tumbler-drying, as compared to a range of 3% shrinkage to 63% stretch with screen-drying. Most of the fabrics shrank from 20% to 25% in area with tumbler-drying, but only 10% to 15% with screen-drying. Thus, tumbler-drying reduced the stretching in width, but increased shrinkage in length and in area.

Only a few of the fabrics which were relaxed by tumbler-drying stretched more than 10% in width; most of them shrank from 8% to 12% in length. Change in area decreased slightly with increase of cover factor, and ranged from 4% stretch to 8% shrinkage.

### *Effect of Geometry upon Elastic Properties*

Load-elongation curves were plotted for all the fabrics. The curve for the fabric knit of 40/1 yarn with 42 courses/inch is presented in Figure 6. The solid lines give the elongation in inches for a 5-in. gage length with and without loads applied perpendicular to the wales. The dotted lines give the contraction along the wales with and without loads applied perpendicular to the wales. From such graphs, calculations were made of the elastic properties.

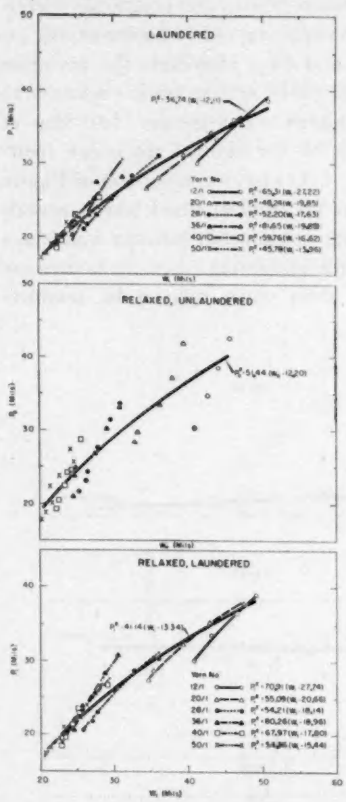


FIG. 5. *The relationship of wale spacings* (w) *to course spacings* (p) *of the finished fabrics: after laundering with tumbler-drying; after relaxation treatment by tumbler-drying; after relaxation treatment by tumbler-drying and laundering by tumbler-drying.* $w_0$ *and* $p_0$ *indicate spacings before laundering;* $w_1$ *and* $p_1$ *indicate spacings after laundering.*

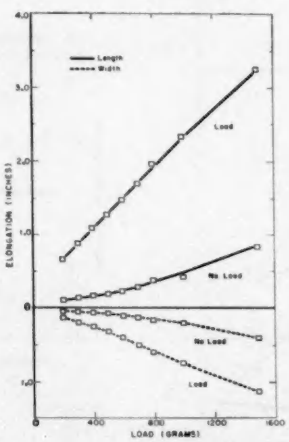


FIG. 6. *Load-elongation curves of fabric of 40/1 yarn and 42 courses/inch, with load applied lengthwise of specimen (perpendicular to wales).*

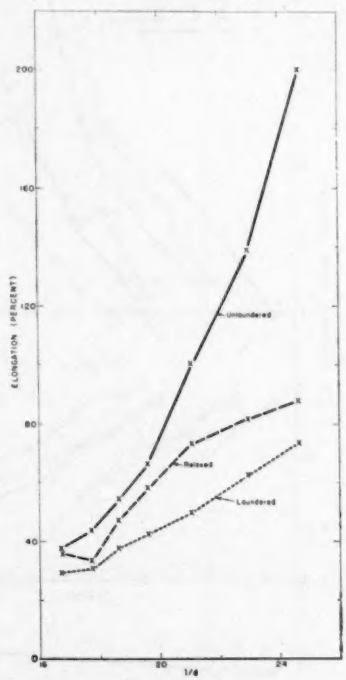


FIG. 7. *Relationship of cover factor* (1/d) *to elongation (700-g. load) of finished fabrics knit with 50/1 yarn: before laundering; after relaxation treatment; and after laundering with screen-drying.*

*Elongation.*—Elongation of the fabrics varied with the relaxation treatment and with laundering. For example, with a load of 700 g. applied perpendicular to the wales, fabrics knit of 50/1 yarn stretched much more before than after laundering (Figure 7). After the relaxation treatment, these same fabrics stretched only slightly more than the laundered fabrics.

The laundered fabrics knit of each yarn exhibited a linear relationship between the cover factor and the elongation. As shown in the cases of 400- and 800-g. loads (Figure 8), the straight lines are approximately parallel and there is considerable displacement between the lines for fabrics knit of 12/1 yarn and of 50/1 yarn. On the other hand, the cover factor-elongation curves for the unlaundered fabrics for the 400-g. load exhibit considerable curvature, which is caused by the distortion of these materials.

*Recovery and permanent set.*—The relationship of elastic recovery to elongation as calculated from the elongation curves (Figure 6) is shown in Figure 9 for fabric knit of 40/1 yarn with 42 courses/inch. The maximum recovery was 84% at 25% elongation. This material, like all the other knit cotton fabrics, decreased in recovery rapidly as the elongation increased. Maximum elastic recovery decreased somewhat, with an increase of cover factor for both unlaundered and laundered fabrics (Figure 10).

At the end of 1 hr. after the last load was released, none of the fabrics had recovered to their original dimensions. The elongation at the end of this pe-

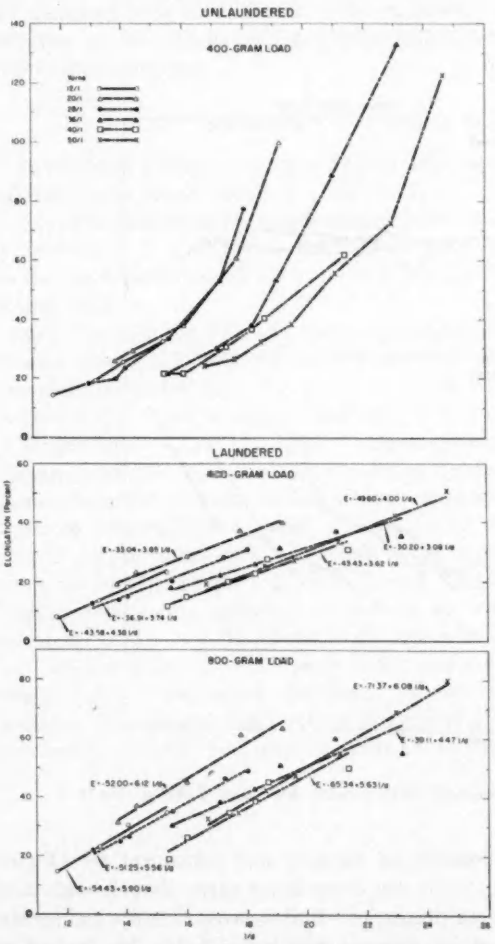


FIG. 8. *The effect of laundering on the relationship of cover factor* (l/d) *to elongation of knit fabrics.*

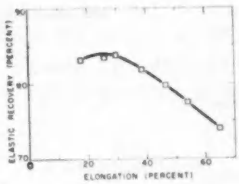


FIG. 9. *Elastic recovery* vs. *elongation of fabric knit of 40/1 yarn with 42 courses/inch.*

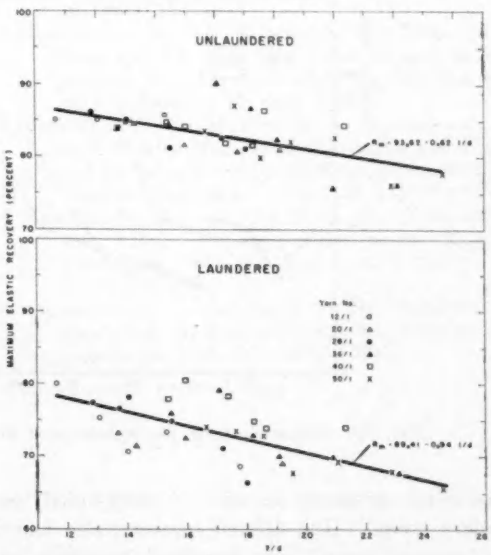


FIG. 10. *Relationship of cover factor* (l/d) *to maximum elastic recovery* ($R_m$) *of unlaundered and laundered fabrics.*

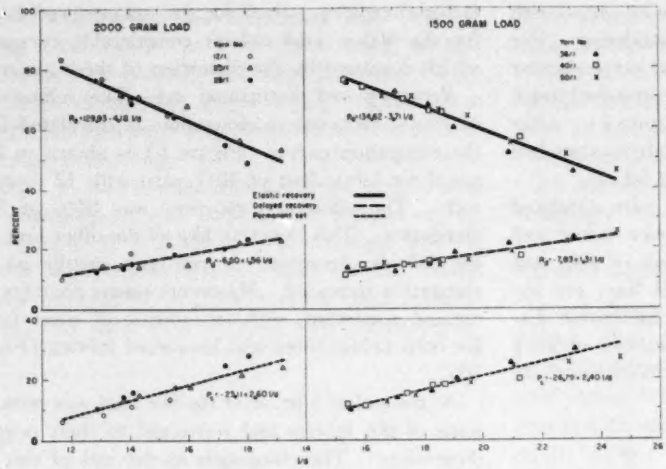


FIG. 11. *Relationship of cover factor* (1/d) *to elastic recovery* ($R_e$), *delayed recovery* ($R_d$), *and permanent set* ($P_e$) *for fabrics knit of 12/1, 20/1, and 28/1 yarns for a 2,000-g. load, and for fabrics knit of 36/1, 40/1, and 50/1 yarns for a 1,500-g. load.*

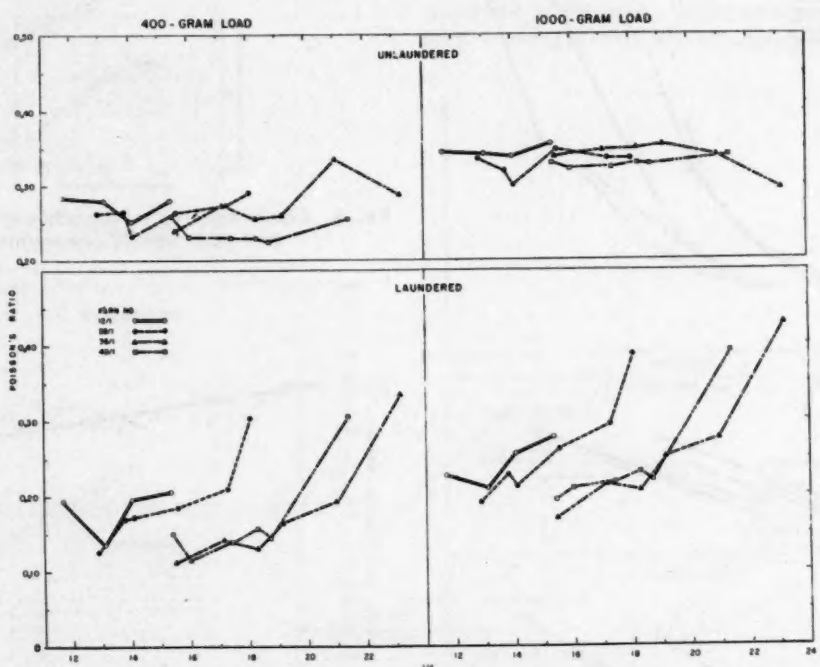


FIG. 12. *Poisson's ratio for unlaundered and laundered fabrics with 400- and 1,000-g. loads.*

riod is the permanent set which is often called "secondary creep." The delayed recovery, also known as "primary creep," was calculated by subtracting the sum of the immediate elastic recovery and the permanent set from the total elongation.

Results for recovery and permanent set (Figure 11) show that cover factor varies linearly with these elastic properties. Both delayed recovery and permanent set increase with cover factor, but immediate elastic recovery decreases with cover factor.

*Poisson's ratio.*—The elongation perpendicular to the wales and the contraction along the wales for different loads were read from curves, such as those given in Figure 6. The ratio of the contraction to the elongation, known as "Poisson's ratio," ranged from 0.22 to 0.33 for a 400-g. load and from 0.30 to 0.36 for a 1,000-g. load for the unlaundered materials (Figure 12). These values are comparable to those given for most metals, which are generally considered to lie between 0.25 and 0.33.

The values of Poisson's ratio for the laundered fabrics ranged from 0.11 to 0.34 for the 400-g. load and from 0.17 to 0.43 for the 1,000-g. load. The ratio for the unlaundered fabrics was independent of the cover factor, but for the laundered fabrics the ratio increased with cover factor. This difference in behavior of the unlaundered fabrics is undoubtedly due to their distortion.

## Summary

In the study of the geometry of 34 plain knit cotton fabrics, it was found that:

(*1*) The data for stitch length ranged from $l = 2p + w + 4.34d$ to $l = 2p + w + 6.37d$, as compared to the theoretical value of $l = 2p + w + 5.94d$ which Peirce derived.

(*2*) The data for wale and course spacings of the fabrics laundered with screen-drying and with tumbler-drying followed the parabolic curve $p^2 = a(w + b)$, in which $a$ ranged from 28.2 to 51.4 and $b$ ranged from $-11.0$ to $-14.1$. Relaxation treatments given the fabric before laundering removed distortion in the structure so that the wale and course spacings followed this equation.

(*3*) All the fabrics shrank in length (11% to 30% with screen-drying, and 15% to 36% with tumbler-drying) and many stretched excessively in width (3% shrinkage to 63% stretch with screen-drying and 6% shrinkage to 44% stretch with tumbler-drying). After relaxation treatment, dimensional changes in length and width in laundering were never excessive, and did not increase with cover factor ($l/d$). Changes were usually less than 10% and many were less than 5%.

(*4*) With stress applied perpendicular to the wales, the strain exhibited a linear relationship with cover factor ($l/d$) for the laundered fabrics. In the case of unlaundered materials in which there was distortion, the strain increased more rapidly with the higher cover factor.

(*5*) Elastic recovery decreased with strain, and maximum elastic recovery decreased with an increase in cover factor ($l/d$). Delayed recovery and permanent set increased with cover factor.

(*6*) Poisson's ratio usually ranged between 0.10 and 0.40. The ratio was independent of cover factor ($l/d$) for the unlaundered fabrics, and increased with cover factor for the laundered ones.

## Acknowledgment

Grateful acknowledgement is made to Elinora Johnson Williams for laboratory assistance, and to Janet Turner Stransky for assistance with laboratory determinations and preparation of data reported in this paper.

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# The Reaction of Cotton with β-Propiolactone in the Presence of Organic Solvents

## Part I: Purified Cotton

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**Abstract**

β-Propiolactone was reacted with purified cotton in the presence of organic solvents. The reaction was found to be affected by time, temperature, and concentration of reagents. Weight gains of upwards of 60% were obtained.

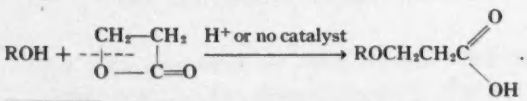
In all reactions of purified cotton with β-propiolactone in organic solvents, etherification occurs, apparently followed by polyesterification of the attached groups by additional lactone. Attempts to direct the reaction towards either etherification or esterification by means of acid and base catalysis were not successful.

Increases in the extent of reaction were obtained by "activation" of purified cotton with acetic acid prior to the treatments with β-propiolactone.

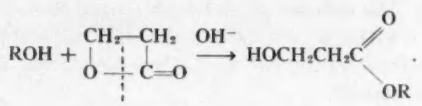
β-PROPIOLACTONE, a relatively new organic compound, was first prepared in 1915 by Johannson from the silver salt of β-iodopropionic acid [7]. The recent discovery of commercial-scale methods of preparing the lactone from ketene and formaldehyde [6, 11] has made it a potentially inexpensive and readily available compound. Jones and Lundgren [8, 9] and Fearnley and Speakman [2] described its use for imparting new and important felting properties to wool. The present study was carried out with the object of determining whether the application of β-propiolactone to cotton would give it new and useful properties.

The lactone, an internal ester of β-hydroxypropionic acid, has the chemical reactivity characteristic of compounds with four-membered rings. It reacts with a variety of compounds, such as water, acids, bases, salts, phenols, amines, mercaptans, acid chlorides, ammonia, alcohols, and others, which gives it a wide range of application.

With no catalyst or in the presence of an acidic catalyst, β-propiolactone reacts with alcohols to form β-alkoxy acids [5]. The lactone ring opens at the oxygen-methylene carbon bond, as follows:

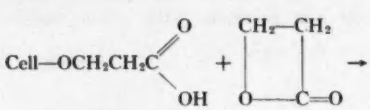



With basic catalysts, the ring opens at the oxygen-carbonyl carbon bond to form esters, as follows:

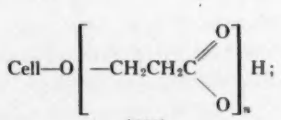



Polymerization of the lactone may also occur in both reactions.

These known reactions of β-propiolactone with alcohols should be equally applicable to cellulose since it is a polyhydric alcohol. According to the reactions given above, the product of the acid-catalyzed or uncatalyzed reaction of β-propiolactone with cellulose should be carboxyethylcellulose (*I*), while basic catalysts should give the hydroxypropionic acid ester of cellulose (*II*). In either case, the newly added —COOH or —OH groups would be available for "anchored" or "graft" polymerization with more lactone, as follows:




(*I*)




(*III*)

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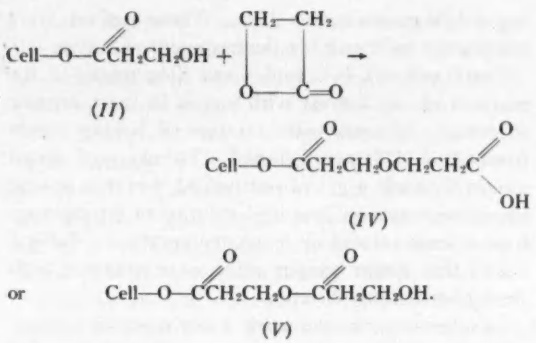
† One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.



(*II*)

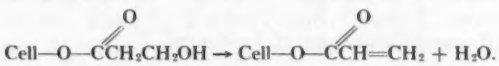


(*IV*)

or 

(*V*)

It should also be possible to dehydrate the ester (*II*) to introduce an unsaturated bond, as follows:



Also, the lactone could polymerize with itself in addition to or instead of reacting with the cellulosic hydroxyl.

Obviously, with the variety of products (*I–V*) capable of being formed during the treatment of cellulose with β-propiolactone, it will not be possible to obtain a clear-cut indication of the course of the reaction under various conditions. It should be possible to compare the weight gain effected with the amount of carboxyethyl groups present, as determined by titration before and after saponification. However, these determinations will yield only a limited amount of information. Since saponification would not be expected to remove groups directly etherified with the cellulose, determination of carboxyethyl groups after saponification would give an indication of the direct etherification. Therefore, the weight loss on saponification should be due to ester cleavage, as in *II*, *III*, *IV*, and *V*. Determination of acid groups before saponification should reveal the free carboxyl groups, as in *I*, *III*, and *IV*. However, it can be seen that from these figures, the proportion of direct and indirect esterification cannot be determined. Furthermore, loss of short-chain soluble material during saponification would make the weight-loss figures less reliable. Although in this study a number of samples were examined exhaustively, the results were not highly informative. For most samples, the amount and kind of reaction was estimated by the weight gain of the treated and extracted cotton and by titration of the acid groups.

Part I of this report describes the reaction of purified cotton cellulose with β-propiolactone in organic solvent solution. Time, temperature, and concentration of reagents were varied to ascertain the best conditions of treatment.

Part II (p. 744, this issue) describes the effects of the presence of the noncellulosic constituents of cotton and of other factors on the reaction. Later papers in this series will report on the reaction of cotton with β-propiolactone in the presence of sodium hydroxide and the properties of β-propiolactone-modified cotton.

## Experimental

### *Materials and Methods*

In preliminary experimentation on the reaction of the lactone with cotton, it was found that large differences in reactivity were obtained, depending upon the state of the cotton used. Such factors as twist, internal tension produced by mercerization, the presence of noncellulosic constituents such as wax, salts, pectinaceous materials, etc., had a definite effect on the extent of the reaction. In some cases the reactivity was increased, while in others it was decreased. Therefore, except where otherwise indicated, the cotton used in these experiments was in the form of 12/5 sewing thread, purified by boiling in ethanolamine for 3 hrs. to remove noncellulosic constituents [10, 12].

β-Propiolactone, obtained from the B. F. Goodrich Chemical Co.,* was distilled at reduced pressure prior to use in the experiments. The lactone is quite stable for some time under refrigeration, but will polymerize when heated.

After reaction of the cotton with β-propiolactone, the treated samples were extracted in a Soxhlet apparatus with acetone to remove unbound polymeric material (known to be highly soluble in acetone [4]) formed during the treatment by side reactions. When treated cotton which had been extracted with acetone was ground to a powder and again extracted, the second extraction did not remove additional polymer. This indicated that the lactone polymer was bound to the cellulose and was not mechanically entrapped within the fibers.

After extraction, the samples were dried in a Dietert dryer * at 105°C for 15 min. and weighed. This time period was shown to be sufficient since the samples did not lose weight when dried for longer

* The mention of trade products and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

times. All weight gains reported in this paper are on a dry basis.

The carboxyethyl content of treated samples was determined by allowing the samples to stand overnight in excess standard 0.1*N* sodium hydroxide and back-titrating with standard hydrochloric acid.

Samples were saponified by heating 1 g. of the treated cotton in 100 ml. of 2% aqueous sodium hydroxide on a steam bath for 3 hrs.

### *Effect of Reaction Media*

*Pure β-propiolactone.*—Reaction of wool with β-propiolactone in the vapor phase has been very successful [9], and this prompted early experiments with cotton along these lines. However, results of the treatment of cotton by the vapor-phase method were discouraging in that only 2.3% weight gain was effected after treatment for 30 min. at 90°C and 30–40 mm. of mercury pressure. When a skein of cotton thread was allowed to stand at room temperature (25°C) in pure β-propiolactone for 18 hrs., the resulting weight gain was only 2.7%. These methods were considered inefficient for the treatment of cotton.

*Inert solvents.*—A study was then made of the reaction of the lactone with cotton in inert organic solvents. Solvents with a range of boiling points from 61°–134°C were selected. Twenty-yard skeins (approximately 4 g.) of purified 12/5 cotton sewing thread were reacted in a 10% solution of β-propiolactone in each solvent at reflux temperature. Table I shows that larger weight gains were obtained with the higher boiling solvents.

In other experiments using water-miscible solvents with comparable boiling points, consistently smaller weight gains were obtained than with the water-immiscible solvents listed in Table I.

TABLE I. REACTION OF COTTON WITH β-PROPIOLACTONE IN ORGANIC SOLVENTS*

| Solvent | Reflux temperature (°C) | Weight gain† (%) |
|---|---|---|
| Chloroform | 67 | 0.5 |
| Petroleum ether | 68 | 2.5 |
| Benzene | 84 | 1.5 |
| Toluene | 108 | 13.5 |
| Xylene | 134 | 29.6 |

* Twenty-yard skeins of purified cotton were refluxed in 100 ml. of 10% solution of β-propiolactone in the indicated solvent for 1 hr.

† After extraction with acetone to remove unbound polymer.

TABLE II. EFFECT OF ACETIC ACID "ACTIVATION" OF PURIFIED COTTON ON THE REACTION WITH β-PROPIOLACTONE*

| Reaction time (min.) | Weight gain† Nonactivated (%) | Activated (%) |
|---|---|---|
| 5 | 3.0 | 10.4 |
| 10 | 5.1 | 19.4 |
| 15 | 8.0 | 26.7 |
| 30 | 13.1 | 36.4 |
| 45 | 20.4 | — |
| 60 | 31.6 | 60.9 |

* Twenty-yard skeins of 12/5 sewing thread were refluxed in 100 ml. of 10% β-propiolactone in xylene.

† After extraction with acetone to remove unbound polymer.

### *Effects of Conditions of Treatment*

As a result of the findings of the above experiments, xylene was used as a reaction medium to determine the effects of such conditions as time, temperature, and concentration of reagents in the reaction of β-propiolactone with purified cotton cellulose.

*Time of reaction.*—The extent of reaction between purified cotton and β-propiolactone was determined by refluxing 20-yd. skeins of purified cotton in 100 ml. of 10% β-propiolactone in xylene for 5, 10, 15, 30, 45, and 60 min. The results obtained, shown in column 2 of Table II and in Figure 1, indicate that, with other conditions constant, the weight gain increases steadily as a function of time.

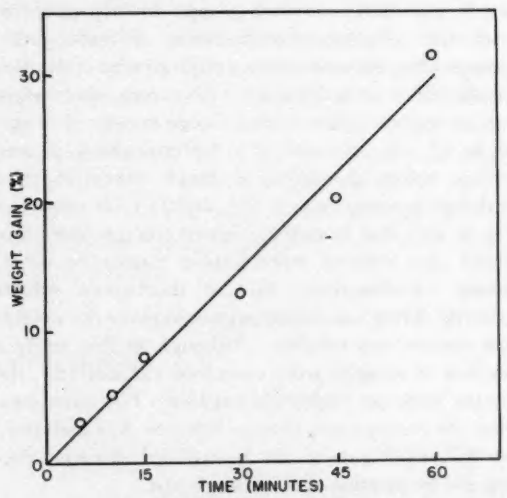



FIG. 1. *The effect of reaction time on the weight gain of cotton treated with β-propiolactone.*

*Temperature of reaction.*—The effect of the temperature on the reaction was determined by a series of experiments in which skeins of dry, purified cotton thread were treated for 1 hr. in xylene containing 10% β-propiolactone at temperature increments of approximately 20°, in the range 42°C to reflux temperature. The results, recorded in Table III, indicate that the higher the temperature, the greater the extent of reaction. Thus, the reflux temperature was found to be the most effective for this reaction.

*Concentration of reagents.*—The optimum concentration of reagents in the reaction between purified cotton and the lactone was determined by refluxing 20-yd. skeins of purified cotton thread in 100 ml. of solutions of β-propiolactone in xylene for 1 hr. The results, shown in Table IV and Figure 2, indicate that the weight gain increases with the concentration of the lactone up to about 20% concentration, and then levels off. Of the concentrations tried, 10% was considered the most efficient for purposes of this investigation.

### *Miscellaneous Effects on the Reaction*

*Effect of swelling.*—Since in most reactions of cellulose it is advantageous to have the cellulose in a preswollen state, it was advisable to determine the effect of swelling on the reaction between purified cotton and β-propiolactone.

A 20-yd. skein of purified cotton thread was swollen by boiling in water containing a wetting agent, solvent-exchanged from water to alcohol to benzene to xylene, and then reacted in a 10% solution of β-propiolactone in xylene at the reflux temperature for 1 hr. The weight gain of the sample was 21.3%, much less than the 29.6% obtained on an ordinary air-equilibrated sample given the same treatment.

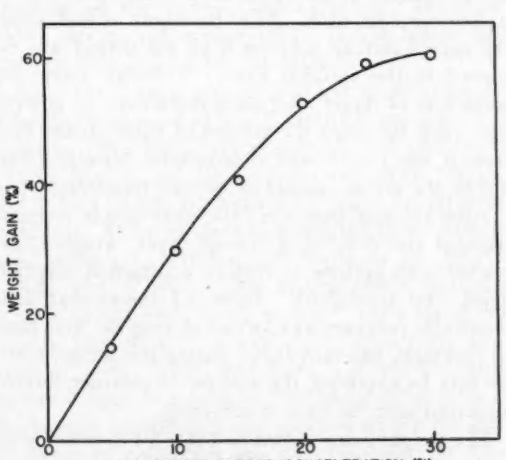



FIG. 2. *The effect of concentration of β-propiolactone on the weight gain of purified cotton.*

*Effect of acetic acid activation.*—Elöd *et al.* [1] reported that acetic acid is an effective "activating agent" for cotton, and acetylation proceeds about ten times faster with than without the pretreatment. Accordingly, a 20-yd. skein of purified cotton thread was soaked in glacial acetic acid for 1 hr. and then extracted with xylene (at room temperature) prior to treatment with 10% β-propiolactone in xylene at reflux for 1 hr. Reaction times of 5, 10, 15, 30, and 60 min. were used. The results of this pretreatment are shown in Table II, and may be compared with those for the nonactivated samples. They indicate that the acetic acid "activation" tripled the amount of reaction up to the 30-min. reaction time, and doubled the amount of reaction obtained in the 60-min. sample. Whether this increased reactivity was due to activation of the cotton, or to catalysis of the polymerization of the lactone after reaction with the cot-

TABLE III. EFFECT OF TEMPERATURE ON THE REACTION BETWEEN COTTON AND β-PROPIOLACTONE

| Reaction temperature (°C) | Weight gain before extraction (%) | Weight gain after extraction* (%) |
|---|---|---|
| 42 | 0.9 | 0.9 |
| 61 | 2.5 | 1.6 |
| 82 | 3.2 | 2.8 |
| 101 | 5.1 | 4.4 |
| 121 | 14.2 | 13.3 |
| 133 (reflux) | 23.8 | 20.2 |

* Samples were extracted with acetone to remove unbound polymer.

TABLE IV. EFFECT OF CONCENTRATION OF REAGENTS ON THE REACTION OF PURIFIED COTTON WITH β-PROPIOLACTONE

| Concentration of β-propiolactone* (%) | Weight gain† (%) |
|---|---|
| 5 | 14.5 |
| 10 | 29.6 |
| 15 | 40.4 |
| 20 | 52.3 |
| 25 | 58.9 |
| 30 | 60.0 |

* In xylene at reflux for 1 hr.
† After extraction with acetone to remove unbound polymer.

ton, or both, is not known. Catalysis by acids and bases is discussed below.

*Effect of moisture.*—According to Jones *et al.* [9], drastically different results were obtained for samples of wool which were dried prior to treatment with β-propiolactone and samples which were treated containing ordinary atmospheric moisture. The effect of atmospheric moisture and added moisture on the reaction of the lactone with purified cotton was investigated. One skein of cotton thread was dried in a Dietert dryer for 15 min. at 105°C, and refluxed in xylene for 2 hrs., during which time any remaining moisture would have been collected in a Stark and Dean trap. The cotton was then reacted with 10% β-propiolactone in xylene at reflux for 1 hr.; the weight gain was 21.8%. Azeotropic distillation of moisture during the reaction had no effect.

A second skein, which contained 5.7% atmospheric moisture, was treated with β-propiolactone in xylene in the same manner. This skein had a weight gain of 29.6%. A third skein was soaked with water containing a wetting agent, washed thoroughly, and then centrifuged to 50% pickup. This moist skein, after treatment with the lactone as above, gained 16.0% in weight, indicating that the excess moisture competed with the cotton in the reaction. Small amounts of moisture, however, seem to enhance the reaction somewhat.

*Effect of acids and bases.*—As mentioned earlier, acids and bases are known to catalyze the reaction between β-propiolactone and alcohols to form ethers and esters, respectively. To determine if the reaction between the lactone and cotton cellulose could be catalyzed in this manner, some organic acids and bases were added to the reaction mixtures.

Twenty-yard skeins of purified cotton thread were refluxed for 1 hr. in 100 ml. of 10% β-propiolactone in xylene to which 1 g. of catalyst had been added. The compounds selected were *p*-toluenesulfonic, oxalic, sulfanilic, and acetic acids, and piperidine, triethanolamine, pyridine, and aniline. With the exception of the *p*-toluenesulfonic acid sample, which caused the β-propiolactone to react explosively, results are shown in Table V.

Weight gains of the samples which had been treated in the presence of piperidine, triethanolamine, and aniline were about normal for an uncatalyzed reaction. It is apparent that the pyridine inhibited the reaction between the lactone and the cotton; however, the carboxyethyl content of this sample was proportionately greater than in the other samples, an effect opposite to what was expected. None of the other catalysts used effectively directed the reaction toward either etherification or esterification as postulated; however, the acetic acid apparently increased the amount of reaction. This may have been due to activation, described previously, or to catalysis of the polymerization reaction.

TABLE V. EFFECT OF ACIDS AND BASES ON THE REACTION OF COTTON WITH β-PROPIOLACTONE*

| Catalyst | Weight gain (%) | Carboxyethyl content (%) | Carboxyethyl / Weight gain |
|---|---|---|---|
| None | 31.6 | 10.62 | 0.34 |
| *Acids* | | | |
| Oxalic | 10.1 | 4.50 | 0.45 |
| Sulfanilic | 12.3 | 5.94 | 0.48 |
| Acetic | 47.5 | 14.27 | 0.30 |
| *Bases* | | | |
| Piperidine | 29.6 | 8.29 | 0.28 |
| Triethanolamine | 28.3 | 8.49 | 0.30 |
| Pyridine | 7.7 | 4.67 | 0.61 |
| Aniline | 20.3 | 7.44 | 0.37 |

* One gram of catalyst was added to 10% β-propiolactone in xylene immediately prior to reaction with cotton for 1 hr. at reflux temperature.

*Effect of successive treatments.*—In order to demonstrate the practicability of reusing lactone solutions, six 20-yd. skeins of dry cotton thread were successively treated in the same 10% lactone solution in xylene for 1 hr. each. After treatment of each skein, the excess lactone solution from the thread was returned to the reaction flask. Although there was some loss of liquid after each treatment, no attempt was made to adjust the volume of liquid in the flask since it was impractical to determine, between treatments, the actual amount of lactone remaining.

After remvoal from the flask, each sample was centrifuged and dried in a Dietert dryer, weighed, extracted with acetone to remove unattached polymer, dried, and reweighed. Table VI shows that little removable polymer was formed during the first hour of refluxing, and only 9.2% during the second hour. As may be expected, the amount of polymer formed increased with the time of refluxing.

The weight gains shown in Table VI decrease with successive samples, probably because of the decrease in available monomeric lactone. According to information received in a prepublication review by

TABLE VI. EFFECT OF REUSE OF β-PROPIOLACTONE-XYLENE SOLUTION*

| Treatment No. | Weight gain before extraction (%) | Weight gain after extraction† (%) | Loss (%) |
|---|---|---|---|
| 1 | 21.9 | 21.7 | 0.9 |
| 2 | 26.2 | 23.8 | 9.2 |
| 3 | 18.7 | 15.0 | 19.8 |
| 4 | 15.9 | 10.3 | 35.2 |
| 5 | 17.4 | 10.9 | 37.4 |
| 6 | 14.7 | 6.2 | 57.8 |

* Six samples of purified cotton thread were refluxed for 1 hr. each in the same 10% solution of the lactone in xylene.
† Samples were extracted with acetone to remove unbound polymer.

Gresham [3], the increasing losses due to extractable polymer might have been reduced by building the lactone concentration up to the original amount before each treatment. In order to maintain continuity of experimental conditions throughout the series of experiments, no attempt was made to do this.

It may be concluded, therefore, that it would be possible to reuse the β-propiolactone solutions, and, with careful control of concentration, loss by polymer formation would not be excessive.

*Composition of Products*

As mentioned above, it is not possible to differentiate completely between the various possible reaction products of the lactone and cellulose. However, added pickup and carboxyethyl content before and after saponification were determined.

Apparently most of the addition takes place by polyesterification of attached carboxyl groups. For example, when three typical samples with pickups of 29.6%, 52.3%, and 60.0% were saponified, 98.6%, 88.5%, and 94.2%, respectively, of these weight gains were lost. Prior to saponification, the three samples had respective carboxyethyl contents of 12.3%, 13.4%, and 17.4%. After saponification and conversion to the acid form, however, titration of the residual free carboxyl groups gave carboxyethyl contents of 4.9%, 7.3%, and 7.5%. From the latter figures it may be concluded that about 12%–17% of the lactone substituents are attached to the cellulose by direct etherification and the remainder by polyesterification.

## Conclusions

It has been determined that cotton will react readily with β-propiolactone in organic solvent solution, and that the reaction is a function of time, temperature, and concentration. It is assumed that the reaction consists of etherification of the cellulose, followed by polyesterification of the attached groups by additional lactone.

Preswelling of the cotton with water, with subsequent solvent exchange, does not enhance the reaction. However, acetic acid activation or catalysis increases the rate and total amount of reaction of the lactone with cotton.

Cotton containing ordinary atmospheric moisture will react slightly better than dried cotton with β-propiolactone, but the presence of excess moisture hinders the reaction.

Attempts to direct the reaction of the lactone with purified cotton towards either etherification or esterification by means of acid or base catalysis did not succeed because of competing reactions of the lactone in the presence of the catalysts.

Xylene solutions of β-propiolactone may be reused, within limits, without excessive polymer formation.

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(*Manuscript received January 4, 1954.*)

# Part II: Raw Cotton


## Abstract

Factors which influence the reaction between raw cotton and β-propiolactone were studied. It was found that the noncellulosic alkaline salts, naturally present in raw cotton, catalyze the reaction and make possible weight gains of over 200%.

Mercerization, increase in twist, and the presence of natural waxes and of excess moisture adversely affect the reaction. The extent of reaction depends upon time, temperature, and the concentration of reagents, as with purified cotton.

Prepolymerized β-propiolactone will not react to any appreciable extent with raw cotton.


ALTHOUGH cellulose constitutes from 88% to 96% of the dry weight of cotton, there are several other important substances, such as wax, pectin, protein, and salts [4, 5, 6, 7], which could exert an effect, either positive or negative, on the reaction of cotton with β-propiolactone. The effects of these components, as well as the effects of other factors, such as twist and the internal tension caused by mercerization, were investigated and are reported below.

### Treatment of Cotton Sliver

To elimiate the effect of twist from the reaction between cotton and β-propiolactone, cotton sliver was used in a series of experiments to determine the effect of the presence of wax, the effect of mercerization without tension, and the effect of removing the noncellulosic constituents of cotton.

Part of the sliver was retained in the raw state; part was mercerized in a 20% solution of sodium hydroxide for 1 hr., washed with water, neutralized with acetic acid, and rewashed; part was extracted with hot acetone to remove waxes; and part was boiled in ethanolamine to remove the noncellulosic constituents, then neutralized with acetic acid, and washed thoroughly with water. After air-drying, each of these four samples were refluxed in 100 ml. of a 10% solution of β-propiolactone in xylene (approximately 25 times the weight of cotton) for 1 hr., extracted with hot acetone to remove unbound polymer, dried and weighed to determine the weight gain.

It was found that the mercerized sample gained 24.2% in weight; the ethanolamine-purified sample gained 42.5%; the raw cotton gained 108.6%; and the dewaxed sample gained 129.6%. These results show that mercerization reduced the amount of reaction considerably. This is possibly the result of two factors working together: (*1*) during the mercerization and subsequent washing, the soluble salts in cotton are removed (the catalytic effect of these salts on the reaction is discussed later); and (*2*) mercerization increases the internal tension in the cotton fibers as a result of swelling. This effect has been observed in work by the authors and others [1, 8]. These results also show that the presence of wax hinders the reaction slightly, although it would be expected to be removed by the boiling xylene. Purification with ethanolamine obviously removes some substance (or substances) which catalyzes the reaction of cotton with the lactone.

### Treatment of Dewaxed Cotton

Cotton which had been dewaxed by extraction with acetone was used in a series of experiments similar to those described in Part I on purified cotton [2] (this issue, p. 738).

#### *Time of Reaction*

Four-gram skeins of dewaxed, 12/5 cotton sewing thread were treated in 100 ml. of 10% solution of β-propiolactone in xylene (approximately 25 times the weight of cotton) at reflux for 5, 10, 15, 30, 45, and 60 min. Weight gains after acetone extraction, drying, and weighing are shown in the second column of Table I and in Figure 1. When these results are compared with those obtained on purified cotton, the catalytic effect of the noncellulosic components of cotton on the reaction becomes apparent.

The effect of twist may be observed by comparing the 78.5% weight gain of the twisted 12/5 thread (60-min. sample) with the 129.6% weight gain of the untwisted sliver described above. The results of a series of experiments confirmed this observation.

#### *Acetic Acid Activation*

Dewaxed, 12/5 cotton thread was "activated" by soaking in glacial acetic acid for 1 hr., and then ex-

tracting with xylene at room temperature prior to treatment with the lactone. Samples weighing approximately 4 g. each were treated for 5, 10, 15, 30, 45, and 60 min. in 100 ml. of a 10% solution of the lactone in xylene at reflux. After treatment, the samples were extracted with acetone, dried, and weighed. Weight gains are shown in the fourth column of Table I.

The acetic acid "activation" did not increase the amount of reaction until after 15 min. time, and then the increases were not as great, proportionately, as those obtained with activated, purified cotton. This may be explained by the possibility that the acetic acid partially removed or neutralized the effect of some of the noncellulosic constituents of the dewaxed cotton. The effects of these constituents are discussed in more detail below.

*Concentration of Reagents*

When dewaxed, 12/5 cotton thread samples were treated in various concentrations of the lactone in xylene, ranging from 5% to 30% by volume, weight gains (after extraction with acetone) increased with the concentration, as shown in Table II. These weight gains are approximately 2 to 3 times as large as those obtained with purified cotton in a like series of experiments.

Figure 2 shows that the weight gain increases apparently as a straight-line function of the concentration.

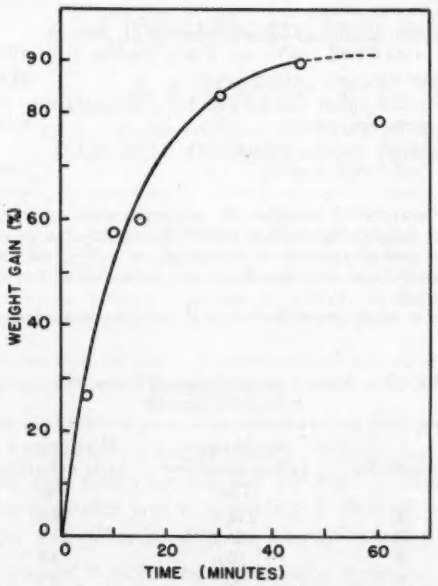


FIG. 1. *The effect of reaction time on the weight gain of raw cotton treated with β-propiolactone.*

## Treatment of Dewaxed, Hot-Water-Extracted Cotton

It has been determined that a typical sample of raw cotton contains about 1.2% of ash, and that this ash is strongly alkaline [5]. Eightly-five percent of this ash can be removed from the cotton by extraction with water [9]. Accordingly, the following samples, consisting of 20 yds. of 12/5 cotton thread weighing approximately 4 g. each, were treated with 10% β-propiolactone in xylene at reflux for 1 hr.: (*1*) dewaxed cotton; (*2*) dewaxed cotton, hot-water-extracted; (*3*) dewaxed cotton, hot-water-extracted,

TABLE I. EFFECT OF ACETIC ACID ACTIVATION ON THE REACTION OF COTTON WITH β-PROPIOLACTONE*

| Reaction time (min.) | Weight gain† Nonactivated Dewaxed (%) | Nonactivated Purified (%) | Activated Dewaxed (%) | Activated Purified (%) |
|---|---|---|---|---|
| 5 | 26.5 | 3.0 | 15.0 | 10.4 |
| 10 | 57.3 | 5.1 | 40.1 | 19.4 |
| 15 | 59.9 | 8.0 | 55.3 | 26.7 |
| 30 | 83.2 | 13.1 | 106.3 | 36.4 |
| 45 | 89.6 | 20.4 | 110.9 | — |
| 60 | 78.5‡ | 31.6 | 114.0 | 60.9 |

* Four-gram skeins of dewaxed 12/5 cotton sewing thread were refluxed in 100 ml. of 10% β-propiolactone in xylene.
† After acetone extraction to remove unbound polymer.
‡ Duplicate samples for 30-, 45-, and 60-min. reaction time gave almost identical results with those shown. The reason for this decrease in the 60-min. reaction time sample is not evident.

TABLE II. EFFECT OF CONCENTRATION OF REAGENTS ON THE REACTION OF DEWAXED COTTON WITH β-PROPIOLACTONE

| Concentration of β-propiolactone* (by volume) (%) | Weight gain† (%) |
|---|---|
| 5 | 28.7 |
| 10 | 70.7 |
| 15 | 108.9 |
| 20 | 135.3 |
| 25 | 177.9 |
| 30 | 224.5 |

* In xylene at reflux for 1 hr.
† After extraction with acetone to remove unbound polymer.

soaked in a solution of 0.58% potassium carbonate and 0.14% sodium carbonate (the percentages of potassium and sodium in this solution correspond approximately to those found in cotton ash), centrifuged to 100% pickup, and dried; (*4*) ethanolamine-purified cotton; (*5*) purified cotton, soaked in 25 ml. of the hot-water extract obtained from 25 g. of raw cotton, centrifuged to 100% pickup, and dried; (*6*) purified cotton, treated with the salt solution as in (*3*). Weight gains of the treated samples, after acetone extraction to remove unbound polymer and drying, are shown in Table III.

The reaction of the lactone with the cellulose is obviously catalyzed by the water extract and, presumably, the alkaline portion of the extract.

### Reuse of β-Propiolactone Solution

In order to determine how much of the β-propiolactone in a xylene solution will react with dewaxed cotton during successive treatments, the following experiment was conducted. Four 20-yd. samples of dewaxed cotton thread, weighing approximately 4 g. each, were refluxed successively in 100 ml. of a 10% solution of the lactone in xylene for 15 min. After each sample was treated, it was drained and the excess lactone solution was returned to the flask. The results are shown in Table IV.

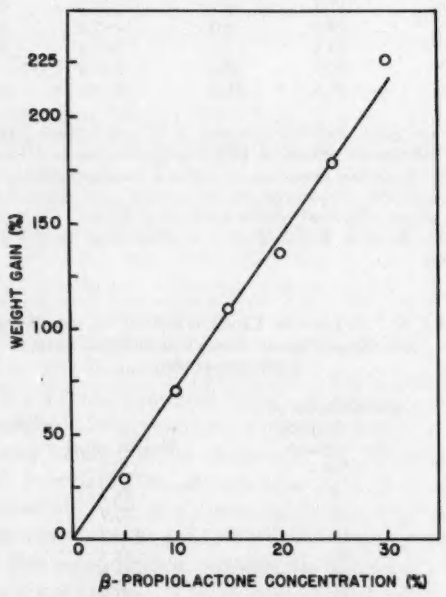


FIG. 2. *The effect of concentration of β-propiolactone on the weight gain of raw cotton treated with β-propiolactone.*

Calculating from these results, the first sample removed approximately 50% of the total lactone, 31% of which was bound to the cellulose and 19% of which was unbound polymer which was extracted by the acetone. The other three samples removed 10%, 4%, and 3%, respectively; of these amounts, 4%, 1%, and 1% were bound to the cellulose and the remainder was unbound polymer. The large amount of free polymer formed was presumably due to catalysis by the salts present in the cotton.

### Treatment with β-Propiolactone Polymer

When a sample of dewaxed cotton thread was refluxed for 1 hr. in 90 ml. of xylene containing 10 g. of β-propiolactone polymer, prepared by catalysis with ferric chloride [3], it gained 32% in weight. When the treated sample was extracted with acetone, however, it retained only 0.47% of the weight gain.

TABLE III. EFFECT OF WATER-SOLUBLE SALTS ON THE REACTION OF COTTON WITH β-PROPIOLACTONE

| Sample* | Weight gain† (%) |
|---|---|
| (*1*) Dewaxed cotton | 78.5 |
| (*2*) Dewaxed cotton, hot-water-extracted | 45.7 |
| (*3*) Dewaxed cotton, hot-water-extracted, treated with 0.58% $K_2CO_3$ and 0.14% $Na_2CO_3$ | 77.9 |
| (*4*) Ethanolamine-purified cotton | 31.6 |
| (*5*) Purified cotton, treated with hot-water extract from raw cotton | 67.5 |
| (*6*) Purified cotton, treated with 0.58% $K_2CO_3$ and 0.14% $Na_2CO_3$ | 93.6 |

* Twenty-yard samples of air-equilibrated 12/5 cotton thread (approximately 4 g. each) were pretreated as shown above, and then refluxed in 100 ml. of a 10% solution of β-propiolactone in xylene for 1 hr., extracted with acetone, and dried.

† After extraction with acetone to remove unbound polymer

TABLE IV. EFFECT OF REUSING XYLENE SOLUTIONS OF β-PROPIOLACTONE

| Sample No. | Weight gain before extraction (%) | Weight gain after extraction* (%) |
|---|---|---|
| 1 | 124.0 | 78.0 |
| 2 | 25.2 | 10.0 |
| 3 | 10.6 | 2.7 |
| 4 | 6.9 | 2.5 |

* Treated samples were extracted with acetone to remove unbound polymer.

This indicated that once the polymer is formed, it will not react with the cotton to any appreciable extent under the conditions described.

### Conclusions

In the treatment of raw and dewaxed cotton with β-propiolactone in xylene, several factors have been shown to influence the amount of reaction, as follows:

(*1*) Twisted cotton will not react to as great an extent as untwisted cotton.

(*2*) Mercerization presumably removes water-soluble catalytic salts and increases the internal tension in the cotton fiber, which decreases the amount of reaction.

(*3*) The presence of natural cotton waxes apparently hinders the reaction.

(*4*) Acetic acid activation does not increase the amount of reaction until after 15 min. of reaction time.

(*5*) The amount of reaction is dependent upon time, temperature, and concentration of reagents.

(*6*) Noncellulosic materials found in cotton, possibly alkaline salts, catalyze the reaction between cotton and β-propiolactone.

(*7*) Polymerized β-propiolactone will not react to any appreciable extent with cotton in xylene at the reflux temperature.

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# Crossbonding of Casein Bristle Fiber*

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### Abstract

A method is described for reducing the rate of water uptake of casein fibers and plastics. The method involves treating formaldehyde-hardened casein products with resorcinol and formaldehyde, drying, and heating. Optimum conditions for this treatment are described. The results indicate that resorcinol forms crossbonds with casein and formaldehyde.

### Introduction

Casein bristle fibers were developed at this laboratory by McMeekin and associates. The process is a simple one, involving only the addition of water to acid-precipitated casein, extruding it through a die heated to 100°C, passing the fibers through a formaldehyde solution, and drying [9]. This process has been utilized commercially to produce casein fiber. The equipment used has been described by Bendigo [1]. Casein bristles are potentially useful in brushes and in the coiled form in upholstery filling, mattresses, and air filters. Casein bristles have satisfactory solvent resistance in oil-base paints, but are softened by the new rubber emulsion paints, which have a water base.

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The patent literature contains numerous claims for the improvement of wool and artificial fibers produced from protein by impregnation with hydrophobic synthetic resins. Since our work was first reported [11], Johnson described the reaction of phenols and formaldehyde with wool [7]. Windus reported data on the acid-catalyzed reaction of resorcinol and formaldehyde with hide substance [16, 17]. The basic reactions involved were described by Fraenkel-Conrat and Olcott in 1948 in a study of the crosslinking of proteins by formaldehyde [5]. In a typical Mannich reaction [2], the $\epsilon$-amino groups of lysine form a methylol, which reacts with the phenol. Our original purpose in investigating these reactions was to determine whether the formaldehyde that had reacted to the methylol stage but had not formed crossbonds [13] would form those bonds if a small amount of an intermediary compound were added. The present paper describes a resin treatment in which substantial amounts of phenols and formaldehyde are bound to the protein fiber and some additional crossbonds are formed.

## Experimental

Casein bristle fiber was produced for this study by continuous production from a screw extruder. The $1\frac{1}{8}$-in. diameter screw was driven by a 2-HP motor at 30 r.p.m. The die was $\frac{1}{4}$-in. thick and contained 10 holes, 0.010-in. diameter, at the delivery end. To reduce the back pressure, however, the holes had a 30° countersink extending within 0.010 in. of the delivery end. The casein mixture was 40% water and 60% high-quality acid-precipitated casein. The threads issued at 300 ft./min. and were drawn off by a rotating drum 10 ft. in circumference. The hot threads from the die fell into a 3% bentonite suspension containing 5% formaldehyde, passed under a roller to change their direction, and then were wound on the wheel. The hardening took place over 24 hrs., while the bristle was drying out on the drum. The finished fiber contained about 3% formaldehyde and had a dry strength of about 0.7 g./den., a wet tenacity of 0.2 g./den., and a denier ranging from 600 to 1200, depending on extrusion conditions.

For the measurement of reagent absorption, the dried bristle was conditioned at 73°F and 50% R.H. for several days and then cut into 9-cm. lengths. Groups of 10 fibers were weighed, placed in a test tube and then used for the various experiments. Following the reaction, the fibers were centrifuged in a basket centrifuge to remove the excess reagent, dried on wire gauze at room temperature, and then heated, usually for 1 hr. at 110°C. From the weight uptake of the fiber, compared with a control which was given only the heat treatment, the amount of reagent absorbed was calculated on the basis of the dry weight.

Tensile strength measurements were made on a Scott IP-2 Serigraph. A 2-in. gage length was used for the wet and dry tests. Fibers measured wet had been soaked for 4 hrs. in distilled water unless otherwise stated. The treated fibers were weighed individually on a microtorsion balance, placed in separate tubes of water, and broken within a few seconds after removal from the water. Chart paper was used to face the clamps of the machine. Knot tests were made with a single overhand knot in the fiber. In order to attain equilibrium quickly, fibers that had been resin-treated and baked were soaked for an hour in distilled water, centrifuged and dried, then equilibrated for 16 hrs. before being tested for knot strength. All figures are the average of 10 individual breaks.

## Results and Discussion

Table I shows the results obtained when casein bristle fibers, hardened with formaldehyde, were immersed in a test tube containing an aqueous 0.01*M*

TABLE I. EFFECT OF ABSORBED PHENOLS ON THE WET TENACITY OF TREATED CASEIN BRISTLE (0.01*M* SOLUTIONS, 16 HRS. AT 25°C)

| Phenol | Uptake, % of substance | Wet tenacity, g./den. after ½ hr. |
|---|---|---|
| Control | — | 0.18 |
| Phenol | 6.6 | 0.17 |
| Metacresol | 16.8 | 0.21 |
| Hydroquinone | 7.2 | 0.17 |
| Catechol | 9.0 | 0.23 |
| Resorcinol | 8.4 | 0.20 |
| 4-chlororesorcinol | 16.1 | 0.40 |
| 4-carboxyresorcinol | 26.6 | 0.38 |
| Pyrogallol | 8.2 | 0.19 |
| Phloroglucinol | 9.3 | 0.26 |
| 4-sulfo-resorcinol | 11.4 | 0.21 |
| 2,2′ 4-4′tetrahydroxydiphenyl sulfide | 7.3 | 0.33 |
| 4-4′dihydroxy diphenyl sulfone (20% EtOH) | 15.8 | 0.21 |
| 4-4′dihydroxy diphenyl sulfide (15% EtOH) | 20.4 | 0.61 |
| $\alpha$-naphthol (20% EtOH) | 17.2 | 0.55 |
| $\beta$-naphthol (20% EtOH) | 16.9 | 0.26 |
| 2,4,2′5′tetrahydroxydiphenyl | 12.6 | 0.21 |

solution of a phenol for 16 hrs. at 23°–25°C. Phenols that were not water-soluble to this extent were dissolved with the aid of 5%–20% ethanol. The fibers were centrifuged and dried at 110°C and the wet tenacity was determined after they were soaked in distilled water for ½ hr. The weight uptake is given on the basis of the oven-dry fiber.

Since the phenol is no longer soluble in water or organic solvents after the baking step, it apparently has reacted with the formaldehyde in the fiber. There seems to be a specific relation between structure and the power to increase the wet strength of the fibers. Metacresol was absorbed in as large amounts as 4-chlororesorcinol and 4-carboxyresorcinol but did not raise the wet strength. 4-4'Dihydroxydiphenyl sulfide and α-naphthol gave good wet strengths, but they have to be applied from alcoholic solution. The sulfone corresponding to the sulfide was absorbed in large amounts but did not increase the wet strength. Although resorcinol itself did not increase the wet strength, three of the compounds that did are resorcinol derivatives. For this reason, the simpler resorcinol was investigated more extensively.

Further evidence of the mechanism of the reaction was sought by studying the stress-strain curve of the resorcinol-treated fiber after it had been soaked for 4 hrs. in distilled water. It showed considerably increased breaking elongation, but no improvement in wet strength. If the added resorcinol is attached to the protein by means of the methylol groups, it is possible that after-treatment with formaldehyde might still further crossbond the protein fiber. To test this idea, fibers were treated in 2% resorcinol solutions for 16 hrs. at room temperature, and without drying were then placed in various concentrations of formaldehyde. After drying at room temperature and heating at 110°C for 1 hr., the fibers were tested. Figure 1 shows the results. The reduction in flow and increase in yield point for the wet fiber clearly indicate that additional crossbonds have been formed. The wet strength calculated from these curves shows that the wet tenacity increased from 0.2 to 0.38 g./den.

A further simplification of this process was possible if the relative reactivities of the phenol and formaldehyde with each other were low, compared with the rate of reaction with the protein. In the absence of added acid or basic catalyst, a solution containing formaldehyde and 1% resorcinol did not precipitate polymer for 2 weeks at room temperature, if the ratio of formaldehyde to resorcinol was 8 to 1 or lower.

Since the reactions of formaldehyde and phenol are catalyzed by acid or base, it appeared likely that an optimum pH might exist for the reaction with casein fiber. Consequently, the effect of pH was investigated. Dilute HCl and NaOH were used to shift the pH of a 1% resorcinol-1.1% formaldehyde solution. With USP formaldehyde and reagent grade resorcinol, the pH value is normally 3.6. After treatment for 16 hrs. at 23°–25°C, the fibers were dried and then heated at 110°C for 1 hr. The results in Table II, indicate that the wet strength of the fiber is optimum over a fairly large pH range. On the acid side the working life of the solutions was greatly decreased and on the alkaline side a deep-brown color due to oxygen absorption was apparent. Since the reaction at pH 3.6 produced a minimum of side reactions between the resin components [15] and did not interfere with the absorption of resin by the fiber, this pH value was used in the remainder of the work. Trial mixtures of formaldehyde and

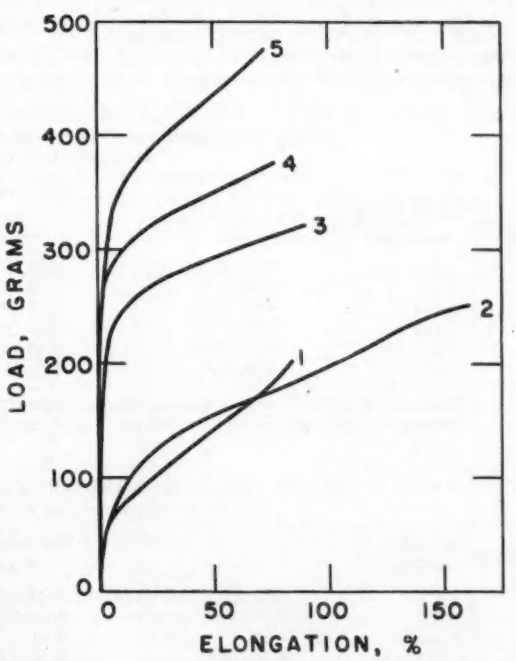


FIG. 1. *Effect of treatment with resorcinol or resorcinol followed by formaldehyde.* (1) *control bristle;* (2)*bristle treated for 16 hrs. in 2% resorcinol;* (3) *same as* (2) *after treatment for 1 hr. in 5% $CH_2O$;* (4) *same as* (2) *after treatment for 4 hrs. in 5% $CH_2O$;* (5) *same as* (2) *after treatment for 24 hrs. in 5% $CH_2O$.*

phenol, metacresol, catechol and hydroquinone, under more acid conditions, did not give the high wet strengths obtained with resorcinol. Paracresol dimethylol and the trimethylol of phenol were also ineffective in increasing wet strength.

The effect of the formaldehyde-resorcinol ratio in the solutions on fiber properties was determined. In addition, the fibers were treated for varying lengths of time, dried at room temperature, and baked at 110°C. Table III shows the regular increase of wet strength and resin content with length of treatment.

At 1:1 ratio, no increase in wet strength accompanied the absorption of resin. A regular increase in resin content with length of treatment was apparent. The higher formaldehyde-resorcinol ratios increased the rate of absorption. High concentrations of formaldehyde alone did not produce any effect.

Precondensation of resorcinol and formaldehyde has been claimed to be of advantage in improving the resistance of wool and casein fiber [8] to water and hot acid dyebaths. When our continuous filament casein fiber [12] was treated with such a resin, the color of the fiber changed slightly to an off-white. In attempting to dye the fiber, contact with the hot acid dyebath changed the color to deep orange-brown. This would certainly be an obstacle to dyeing any color except brown or black. When casein bristle was treated with such a resin, the color of the bristle after heating was tan or brown, the same as with the uncondensed resin. The initial absorption of resin proceeded at a higher rate than that for the uncon-

TABLE II. EFFECT OF pH OF RESORCINOL-FORMALDEHYDE SOLUTIONS ON WET STRENGTH OF CASEIN BRISTLE

| pH | Wet tenacity, g./den. at 4 hrs. | Resin uptake (%) | Aging of solution at 16 hr. |
|---|---|---|---|
| 1.6 | 0.22 | 9.7 | Pink precipitate |
| 2.0 | 0.20 | 12.3 | White precipitate |
| 2.3 | 0.20 | 14.7 | Hazy |
| 2.8 | 0.26 | 13.5 | Clear |
| 3.6 | 0.29 | 14.0 | Clear |
| 5.2 | 0.28 | 13.6 | Clear |
| 5.6 | 0.28 | 13.8 | Tan |
| 6.6 | 0.11 | 11.2 | Brown |
| Control fiber | 0.18 | — | — |

TABLE III. EFFECT OF FORMALDEHYDE-RESORCINOL RATIO ON WET STRENGTH AND RESIN UPTAKE OF CASEIN BRISTLE*

| Ratio formaldehyde† / resorcinol | Wet tenacity, g./den. after 4 hrs. in $H_2O$ | | | |
|---|---|---|---|---|
| | 1 hr. in resin | 22 hrs. in resin | 52 hrs. in resin | 160 hrs. in resin |
| 1:1 | 0.22 (2.1) | 0.25 (7.4) | 0.26 (9.8) | 0.23 (11.9) |
| 3:1 | 0.29 (1.7) | 0.29 (8.8) | 0.30 (10.2) | 0.42 (13.4) |
| 6:1 | 0.28 (2.6) | 0.33 (9.0) | 0.40 (10.9) | 0.57 (14.6) |
| 12:1 | 0.30 (2.8) | 0.41 (9.5) | 0.44 (13.6) | 0.69 (15.9) |
| 18:1 | 0.30 (3.0) | 0.49 (10.3) | | |
| 24:1 | 0.30 (1.8) | 0.53 (11.0) | | |

* Resin uptake is given in parentheses after wet strength.
† Resorcinol concentration kept constant at 1%; formaldehyde was varied.

TABLE IV. EFFECT OF FORMALDEHYDE-RESORCINOL RATIO OF PRECONDENSED RESINS* ON WET STRENGTH AND RESIN UPTAKE† OF CASEIN BRISTLE

| Ratio formaldehyde / resorcinol | Wet tenacity after 4 hrs. soaking g./den. | | | |
|---|---|---|---|---|
| | 1 hr. | 22 hrs. | 54 hrs. | 144 hrs. |
| 1:1 | 0.22 (6.0) | 0.24 (11.0) | 0.25 (11.5) | 0.29 (15.5) |
| 2:1 | 0.23 (7.5) | 0.27 (12.0) | 0.31 (17.0) | 0.42 |
| 4:1 | 0.24 | 0.31 | 0.34 | — |
| 6:1 | 0.28 (10.0) | 0.36 (13.5) | 0.40 (15.5) | 0.61 (16.0) |
| 12:1 | 0.28 (2.0) | 0.46 (10.1) | 0.55 (13.1) | — |
| 18:1 | 0.27 (1.7) | 0.43 (8.4) | — | — |
| 24:1 | 0.28 (1.5) | 0.54 (9.9) | — | — |

* Precondensed resin was made by heating the resorcinol and the formalin solution, 39.5% wt./v., together for ½ hr. at 60°C and then diluting to 1% resorcinol concentration [8]. Dr. Halwer of this laboratory estimated by light-scattering measurements that an 8.8:1 resin had an average molecular weight of 400 ± 100 after ½ hr. of condensation.
† Resin uptake is given in parentheses after fiber tenacity.

densed components. As shown in Table IV, however, the wet tenacities were usually within the standard deviation, 0.03 g./den., of the corresponding value in Table III, when the precondensation step was omitted.

As the ratio of formaldehyde to resorcinol increased, the absorption of the resin passed through a maximum and then decreased. This was not true of the uncondensed series and probably indicates that the higher molecular weight of the resin was cutting down the rate of penetration into the fiber. The precipitability of the resin by dilution with water is also a measure of its size. When USP Formalin, 30 ml., and resorcinol, 5 g., were heated together at 60°C, (molar ratio 8.8 to 1), after 4½ hrs. heating the resin clouded when 50 ml. of water was added. After 6½ hrs. heating, 1 ml. of the resin clouded with 5 ml. of water and precipitated with 6 ml. Precondensed resins were not studied further, since the wet strengths were no better than those shown in Table III and because of the much shorter working life of the solutions.

The effect of the resin on dry tenacity and flexibility must be considered when treated bristle is to be used in brushes. With a low formaldehyde-resorcinol ratio some of the bristles were brittle when the resin content exceeded 10%. High concentration of the resin in the treating solution had the same effect. Fibers were treated for 1 hr. with solutions containing high ratios of formaldehyde to resorcinol, and then dried and baked at 110°C for 1 hr. Table V shows the decrease in flexibility with increase in resorcinol concentration.

In this series the best water resistance and flexibility were obtained at 1% resorcinol concentration. Lower concentrations showed no improvement. Another factor in the brittleness of the fiber is overheating during the baking process. A series of bristle fibers was treated in a 5% resorcinol solution with 6 to 1 formaldehyde-resorcinol ratio for 16 hrs. at room temperature and then dried at room temperature. The effect on flexibility when the fibers were baked at various temperatures is shown in Table VI.

Little improvement in wet strength resulted until the fibers were heated above 65°C. Because of the high resin content, however, the flexibility was impaired even when the fibers were dried at room temperature. In a water-resistant surface coating for protein plastics this lack of flexibility would be of less consequence than in fibers.

TABLE V. EFFECT OF RESORCINOL CONCENTRATION ON FLEXIBILITY OF CASEIN FIBER

| Resorcinol concentration in solution (%) | Ratio formaldehyde / resorcinol | Dry tenacity (g./den.) | Flexibility† (%) | Wet 4 hrs., tenacity (g./den.) |
|---|---|---|---|---|
| 1.0 | 24:1 | 0.57 | 100 | 0.43 (4.2)* |
| 2.0 | 24:1 | 0.75 | 93 | 0.37 (7.6) |
| 3.0 | 24:1 | 0.76 | 90 | 0.33 (8.6) |
| 5.0 | 24:1 | 0.74 | 88 | 0.30 (7.1) |
| 7.5 | 12:1 | 0.78 | 80 | 0.34 (11.4) |

* Resin absorbed.

† Ratio $\frac{\text{tenacity knotted fiber}}{\text{dry tenacity}}$.

TABLE VI. EFFECT OF HEATING ON PROPERTIES OF CASEIN BRISTLE

| Temperature (°C) | Dry tenacity | Flexibility (%) | Wet tenacity (g./den.) | Resin (%) |
|---|---|---|---|---|
| 25 | 0.61 | 68 | 0.22 | 24.4 |
| 35 | 0.69 | 56 | 0.21 | 23.2 |
| 45 | 0.75 | — | 0.21 | 23.3 |
| 55 | 0.67 | 42 | 0.23 | 27.9 |
| 65 | 0.60 | 39 | 0.25 | 26.6 |
| 75 | 0.74 | — | 0.40 | 24.6 |
| 85 | 0.83 | — | 0.73 | 26.0 |
| 95 | 0.85 | — | 0.68 | 25.5 |

TABLE VII. EFFECT OF RESIN TREATMENT ON PROTEIN DISCS HARDENED WITH FORMALDEHYDE

| Protein | Treating solution: Resorcinol (%) | Treating solution: $CH_2O$ (%) | Resin uptake (%) | Water absorption at 24 hrs. (%) | Water absorption at equilibrium (%) | Days to reach equilibrium |
|---|---|---|---|---|---|---|
| Casein | 0 | 0 | 0 | 33.0 | 34 | 3 |
| Casein | 5.0 | 6.4 | 11.0 | 2.5 | 22.6 | 11 |
| Casein | 14.3 | 32.5 | 11.6 | 2.2 | 23.2 | 16 |
| Casein | 25.0 | 29.0 | 13.3 | 1.4 | 21.9 | 23 |
| Soybean | 0 | 0 | 0 | 19.0 | 19.8 | 2 |
| Soybean | 25.0 | 29.0 | 11.4 | 1.25 | 19.4 | 20 |
| Zein | 0 | 0 | 0 | 12.7 | 15.5 | 5 |
| Zein | 5.0 | 5.5 | 14.5 | 4.7 | 15.8 | 8 |

TABLE VIII. EQUILIBRIUM SWELLING OF RESIN-TREATED CASEIN BRISTLES

| Resin content (%) | Moisture at equilibrium (%) | Swelling ratio* |
|---|---|---|
| 0 | 33.2 | 1.64 |
| 5.2 | 30.4 | 1.58 |
| 8.7 | 27.6 | 1.51 |
| 16.2 | 23.5 | 1.41 |
| 23.4 | 20.0 | 1.33 |
| 25.2 | 18.0 | 1.29 |
| 28.5 | 20.4 | 1.34 |

* Ratio $\frac{\text{swollen volume}}{\text{original volume}}$.

Two-inch diameter discs were molded from powdered casein, soybean protein, and zein that had been previously hardened with formaldehyde and contained about 10% water [6]. The discs were placed in resorcinol-formaldehyde solutions (Table VII) for 16 hrs. at room temperature and then dried at room temperature and baked at 100°C for 2 hrs. The effect on water absorption of the discs, which were only $\frac{1}{8}$ in. thick and reached equilibrium rapidly [10], was considerable.

The treatment discolored the discs, but the addition of sodium bisulfite to the treating solutions will decrease the amount of brown color generated during the heating process. Cross sections of the discs showed that the brown color was in the outer part of the discs. Measurements for density were made in organic liquids by N. J. Hipp, of our laboratory, on samples taken by milling the discs to different depths. They showed that the the outer layers were more dense, 1.324–1.333, and probably contained more of the treating resin than the average composition indicated. The inner part of the discs had a density of about 1.283. Resin prepared by evaporation and baking of an 8:1 resin had a density of 1.386.

Since we had observed that the wet strength of casein bristles is lowered by increasing the soaking times to more than 4 hrs., a test was applied to see whether actual additional crossbonds were formed or whether there was merely dilution with a nonabsorbing resin which decreased the rate of water uptake.

A series of casein fibers was treated with a solution containing 5% resorcinol and a 6/1 ratio of formaldehyde for various lengths of time. The bristles contained from 4% to 28.5% resin. When these fibers were allowed to stand in water for 3 days

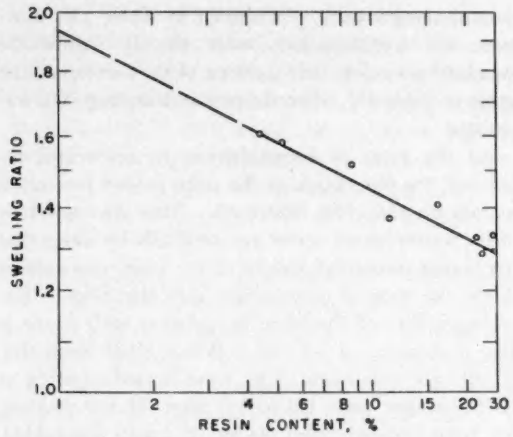


FIG. 2. *Test for crossbonding. Log/log graph of swelling ratio against resin content of casein bristle fiber.*

the maximum swelling was reached. By rapidly wiping the fiber, weighing it at 15-sec. intervals and extrapolating to zero time, a series of values was obtained for equilibrium water uptake. At 48 hrs. the water uptake reached the values given in Table VIII.

Preston and Nimkar [14] used the log of the swelling ratio plotted against log of the resin content as a test for crossbonding. This is based on the Flory-Rehner theoretical equation for equilibrium swelling of a crosslinked polymer [4]. For this purpose the equation can be reduced to $-V_0 = \text{constant} \times M_c^{3/5}$, where $V_o$ is the swelling ratio (swollen volume/original volume) and $M_c$ is the weight of the polymer chain between crosslinks. For slightly crosslinked styrene-divinyl benzene gels, it has been shown by Boyer and Spencer [3] that $M_c = k\ c^{-a}$, where $c$ is the concentration of the crosslinking agent. As shown in Figure 2, the slope of the plot is $-.074$, so $a$ is $-.1235$, and thus the new crosslinkages introduced are proportional to the eighth root of the resin concentration.

When data relating wet strength to resin content were plotted, it was found that increases in the formaldehyde-resorcinol ratio up to 12 to 1 produced higher wet strengths for the same amount of resin, but that increases above this amount produced no further improvement. Other phenols produced more efficient resins, notably 4-4′dihydroxy-diphenyl sulfide. Phloroglucinol reacts too rapidly with formaldehyde for use in a mixed solution. Treatment of

TABLE IX. RELATIVE STIFFNESS OF CASEIN BRISTLES

| | Modulus of stiffness* (in./lbs.) | |
|---|---|---|
| | Wet | Dry |
| Casein, formaldehyde-hardened | $1.04\times10^4$ | $10\times10^4$ |
| Casein, resin-treated | $3–4\times10^4$ | $14\times10^4$ |
| Hog bristle | $7\times10^4$ | $40\times10^4$ |

* When bristles are soaked in water for short periods, values for stiffness will be higher than the figures given here.

a formaldehyde-hardened bristle with phloroglucinol, alone, and then with formaldehyde resulted in absorption of a substantial amount of resin.

Substitution of other aldehydes for formaldehyde produced no improvement. Glyoxal, malonaldehyde, and succinaldehyde were used with resorcinol. Succinaldehyde produced about equal wet strengths; glyoxal and malonaldehyde were inferior. Acetone and furfural did not raise the wet strength.

A quality of bristles directly related to their performance in brushes can be evaluated by measuring the stiffness of wet single bristles on the Olsen-Tour-Marshall stiffness tester. Although the wet stiffness of the bristle was low, the modulus could be computed at equilibrium swelling by using a span of only $\frac{1}{8}$ in. and the lowest range, .05 in.-lb. Table IX shows the results.

## Conclusions

The optimum conditions for reaction of resorcinol and formaldehyde with casein bristle fiber hardened with formaldehyde are: (*1*) high formaldehyde/resorcinol ratio, 12/1 or higher; (*2*) absorption at room temperature; (*3*) pH of 3.6; (*4*) baking temperature of 75°–110°C. With these conditions, the wet strength of treated fibers is raised considerably up to 4 hrs. of soaking in water. If the soaking is prolonged, the resin treatment considerably increases the time required to reach equilibrium. The ultimate wet strength is increased by 50% over the control, however, regardless of the time of soaking.*

* Mention of any specific equipment or products in this paper does not imply that these products are endorsed or recommended by the U. S. Department of Agriculture over others not mentioned.

## Acknowledgment

We are indebted to Mr. N. J. Hipp for density measurements on resin-treated discs, and to Dr. Murray Halwer for light-scattering measurements on the resin solutions.

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(*Manuscript received January 27, 1954.*)

# Letters to the Editor

**Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.**

## Some Observations on the Rigidity of Jute, Ramie, and Sisal

INDIAN CENTRAL JUTE COMMITTEE
Technological Research Laboratories
Regent Park
Calcutta, India
March 27, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

In the course of an investigation of the torsional rigidity of filament, by a previously described method [5], certain interesting observations were made relating to jute, ramie, and sisal. In each case the measurement was made on two groups of 100 filaments, the groups possessing two different values of mass per unit length. The cross-widths of a filament required in this connection were measured [4] at 45° intervals round the perimeter of a cross section. As the rigidity calculation was based on an elliptic cross section, the first and the third observations were considered for each filament to represent the two axes. The rigidity of the 100 filaments of a group was thus found individually, and the mean rigidity was obtained. Taking the mean of the corresponding cross-width observations for all the filaments, the four average cross-width values were obtained for a group. These were used to secure a geometrical representation of the area of cross section from which the total porosity, including lumen, was estimated [7]. The true density for this purpose was found by the method given for jute [2]. The results are summarized in Table I.

The points of interest noticed were as follows: (*1*) Only in the case of materials which yielded a conscionable difference in porosity—*e.g., capsularis* jute and ramie—there occurred a significant difference in rigidity, the heavier filament with higher porosity recording a lower value. One possible cause seems to be that the heavier individuals are, in these cases, mostly made up of composite bodies of such single entities as form a unitary structure after retting [1]; these bodies so closely adhere to each other under the binding action of the interstitial cementing matter that they are physically unseparated during

TABLE I

| Fiber | Mass per unit length (μg./cm.) | R.H.* (%) | Coeff. Var. (%) | Mean area of cross section of filament ($10^{-6}$ sq.cm.) | True density (g./cc.) | Approx. total porosity (including lumen) (%) | Mean rigidity modulus in 79% R.H. ($10^9$ dynes/cm.$^2$) |
|---|---|---|---|---|---|---|---|
| *C. olitorius* (jute) | 16.20±0.027 | 79 | 1.7 | 18.233 | 1 437 | 38.2 | 4.17±0.281 |
| | 20.33±0.031 | 79 | 1.5 | 23.546 | 1.437 | 39.9 | 3.77±0.292 |
| *C. capsularis* (jute) | 11.60±0.029 | 79 | 2.5 | 12.537 | 1.421 | 34.9 | 5.06±0.377 |
| | 15.49±0.026 | 79 | 1.7 | 18.253 | 1.421 | 40.3 | 3.99±0.259 |
| *B. nivea* (ramie) | 8.49±0.029 | 73 | 3.4 | 7.038 | 1.494 | 19.3 | 6.91±0.510 |
| | 12.50±0.030 | 73 | 2.4 | 11.296 | 1.494 | 25.9 | 4.80±0.481 |
| *Agave* (sisal) | 45.0 ±0.06 | 73 | 1.3 | 41.013 | 1.476 | 25.7 | 4.73±0.248 |
| | 57.9 ±0.05 | 73 | 2.4 | 52.204 | 1.476 | 24.9 | 5.03±0.228 |

* The values of jute corrected on the basis of regain data were reported earlier [6].

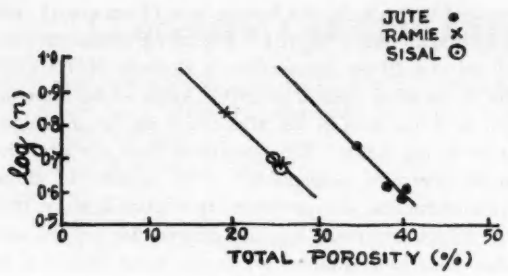


FIG. 1

filamentation. The interstitial cement, due to its wholly amorphous nature, must possess greater porosity than the single entities themselves. The overall porosity of the individual thus increases bringing about the reduction in rigidity. (*2*) When the porosity is plotted against the logarithm of rigidity measured in billion dynes/cm.$^2$, jute and sisal seem to exhibit a characteristic difference (see Figure 1). These two fibers show a distinct segregation of points into separate porosity regions. The cause may be traced to Marsh's finding [3] of larger pore diameter of ramie (80 – 135 Å.) than that of some cellulose and protein fibers (50 – 60 Å.). Sisal is now found to group with ramie and differently from jute.

Further study is on hand and will be reported at a later date.

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S. K. BOSE

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# Directional Triboelectric Effects of Wool and Hair*

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To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

In 1941, Martin [2] observed that when the root end of a wool fiber is pulled from a bundle in which all the fibers are aligned with root ends together, the fiber is charged positively; when the tip end is pulled out, the fiber is charged negatively. Furthermore, if a fiber aligned opposite to those in the bundle is pulled out in either direction, it is uncharged. Since Martin gave only qualitative results, it was decided to make a quantitative investigation with an apparatus to rub together fibers or fiber assemblies under controlled mechanical and ambient conditions. This apparatus, briefly described previously [1], will be discussed more fully elsewhere.

To make sure that one rubbing was not affecting the results of a subsequent rubbing by scale destruction or other mechanism, the following procedure was used: Five degreased wool fibers with the positions of the root and tip ends known were mounted in each of four top yokes and four bottom yokes of the apparatus. Thereby four pairs of samples were available, each pair of which was rubbed together over a *2*-cm. length. The first pair was rubbed together successively in the four directions *1, 2, 3, 4,* as shown at the top of Figure 1, wherein each fiber is supposed to lie in the plane of the paper. The second pair was rubbed in the sequence *2, 3, 4, 1,* and so on.

The data obtained are given in Figure 1, which shows a fairly high positive charge for direction *1*, a smaller negative charge for direction *4*, and small positive charges for rubs *2* and *3*. The charge given is that developed on the bottom fiber. Rubs *1* and *4* correspond to Martin's pulling a fiber out of the bundle so as to create a positive and a negative charge, respectively, on the bottom fibers. Rubs *2* and *3* correspond to those pulls in which no charge is pro-

* This letter is based on a part of the dissertation submitted by S. P. Hersh in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

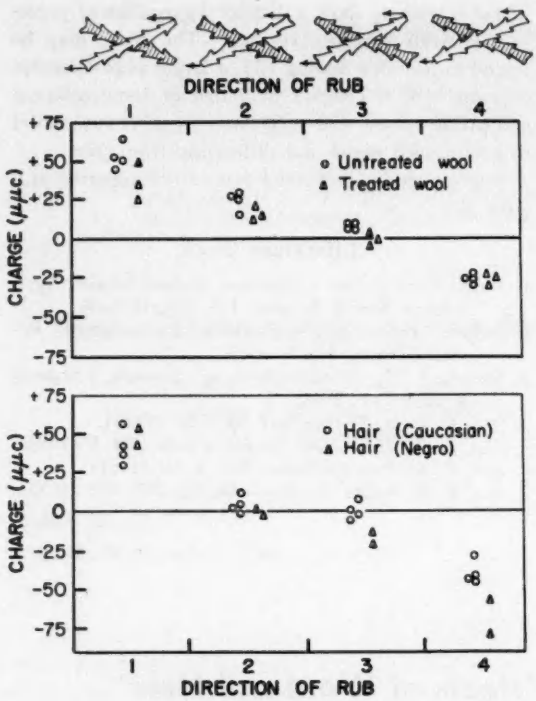


FIG. 1. *Effect of direction of rubbing on charge generated on wool and hair.*

duced. These results therefore agree with the qualitative results of Martin, except for the small charging in rubs *2* and *3*. It will be noted that if a charge of about 10 to 12 micromicrocoulombs were to be subtracted from the charges found, rubs *1* and *4* would produce charges equal in magnitude, and rubs *2* and *3* would be nearly zero.

The experiment was repeated using (*1*) wool treated with alkali, (*2*) human hair (Caucasian), and (*3*) human hair (Negro). The alkali treatment consisted of a 20-sec. immersion in alcoholic KOH (7% KOH in ethyl alcohol at 25°C) followed by immediate neutralization in 5% acetic acid and an overnight wash in tap water. This treatment does not alter the scale contours perceptibly. The results of these measurements, also presented in Figure 1, show that the alkali treatment has not altered the results and that both hair samples show the same behavior as did wool except that the 12-micromicrocoulomb bias is now absent.

These results can be pictured by considering the "slopes" of the scales to be triboelectrically positive to the "points" of the scales. In rub *1* the points of the top fiber move into the slopes of the bottom fiber, which therefore becomes positive. In rub *4* the slopes of the top fiber move into the points of the bottom fiber, which now becomes negative. In rub *2* the slopes move into slopes, in rub *3* the points into points, and the transfer of charge is zero. We have been unable to find any plausible explanation for the different triboelectric behavior of the slopes and points.

We wish to thank Dr. E. H. Mercer for suggesting these experiments and to express our gratitude to the Carbide and Carbon Chemicals Company who sponsored the Participating Fellowship at Textile Research Institute under which this work was conducted.

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S. P. HERSH
D. J. MONTGOMERY

# Concentric Cellulose Layers in Cotton Fiber Cell Wall

Southern Regional Research Laboratory
Southern Utilization Research Branch
New Orleans, La.
May 4, 1954

To the Editor
Textile Research Journal

*Dear Sir:*

Observations with the light microscope of the swelling patterns of cotton fibers treated with cuprammonium hydroxide, or other swelling agents for cellulose, have long been used to demonstrate that the cellulose of the fibers is laid down in concentric layers. However, concentric structures of the type seen in swollen fiber cross sections seldom, if ever, have been visualized with the light microscope in unswollen material. Recently, Kling and Mahl [2], on the basis of electron microscope studies of replicas of the face of cotton fiber cross sections, have argued that the concentricity of the layers is largely distorted or destroyed when the fiber dries after opening of the boll.

In connection with studies of cellulose structure in untreated and modified cotton at this Laboratory, electron microscopical observations have been made on ultrathin cross sections of fibers. Fibers were embedded by polymerization in a mixture of butyl and methyl methacrylates, and sections cut on a modified rotary microtome, using a glass edge [2]. The polymethacrylate was cautiously removed from the sections with methyl ethyl ketone or toluene, and the specimen metal-shadowed prior to examination. The appearance of a typical cross section of untreated cotton is shown in Figure 1. While certain features of the fiber are readily recognizable, such as the lumen and the primary wall (seen torn at the lower edge of the section), structural layers concentric to the lumen are less apparent. A careful study of such micrographs, however, permits the observer to recognize the presence of numerous contiguous layers whose concentricity is only occasionally apparent; the layers are extremely thin, and are ruffled rather than smooth, presumably as a result of shrinkage of the cell wall.

Methacrylate embeddings of partially acetylated cotton fibers [1] (*ca.* 25% acetyl content) result in cross-sectional swelling of the fibers to some 200%–400% of their original size. The swelling is accompanied by separation of the cell wall into con-

Fig. 1. *Electron micrograph of cross section of untreated cotton fiber. Palladium shadowing.*

Fig. 2. *Photomicrograph of cross sections of partially acetylated cotton fibers embedded in polymethacrylate (400 ×).*

FIG. 3. *Electron micrograph of portion of cross section of partially acetylated cotton fiber after removal of methacrylate embedding medium. Palladium shadowing.*

FIG. 4. *Electron micrograph of portion of cross section of partially acetylated cotton fiber after removal of methacrylate embedding medium. Palladium shadowing.*

centric patterns. Figure 2 is a photomicrograph of a cross section of several such embedded fibers. Note that the cell-wall thickness (lumen to periphery) is about 20 $\mu$, while the unswollen fiber cell wall is about 4 $\mu$ thick. When the methacrylate is removed in order to gain the necessary contrast, the appearance of such sections in the electron microscope is that shown in Figures 3 and 4. In Figure 3 the portion of the section shown indicates that the fiber has been distended to some 4 times its original size, and individual groups of fibrils are seen arranged concentrically. Figure 4 shows a region of a somewhat thicker section at higher magnification. In contrast to fiber cross sections swollen in cuprammonium under the light microscope, which show only periodic variations in density, these pictures seem to indicate that the swelling medium actually separates concentric rings of unswollen or little swollen fibrillar material. Considering the high swelling of the fibers, the fibrils making up the concentric arrangements show strong lateral cohesion. The fibrils lie in the plane of the supporting film because the removal of the methacrylate between the groups permits them to fall. The number of layers along any given radius of the fiber section is difficult to estimate, but appears to be about 20–30 or more in many of the specimens examined. Diameters of the individual microfibrils range down to 60 Angstrom units.

Swelling of the partially acetylated fibers in the methacrylate takes place prior to polymerization, but the distention of the cell wall may be enhanced by osmotic systems set up between polymer and monomer—that is, differential rates of polymerization on two sides of the cellulosic membrane would give rise to an osmotic cell. Distention of the fiber with little or no increase in cell-wall thickness has been observed when the fibers are embedded by styrene polymerization, where the embedding medium presumably has no affinity for the ester groups of the acetylated regions of the fiber. Concentric separation of the wall does not appear to occur in styrene embeddings.

The phenomenon reported herein may be useful for studies where it is desirable and possible to break down the organization of the fiber cell wall.

The authors are grateful to Tulane University Biophysics Department and Charity Hospital, New Orleans, La., for the use of the electron microscope.

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VERNE W. TRIPP
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# INDUSTRIAL SECTION

## Fiber Blending*

**G. V. Lund**

*Courtaulds Inc., Mobile, Alabama*

**Abstract**

This paper discusses the inherent "greatest intimacy" of blending possible in a blend yarn of a particular construction, the effect of processing differences on the "intimacy" of a blend, and the factors involved in long-term variation of the composition of a blend yarn, and suggests how the quality of blend yarns may be controlled.

THE DAYS when only a very few natural fibers were available, all with well-known properties, are over. Today many fibers, natural and man-made, all with strengths and all with weaknesses, are available, and the fabric designer, in order to obtain the best fabric for a particular purpose at a price suitable for that purpose, often finds that he can obtain the best result by blending fibers so as to obtain a mixture of the characteristics of the individual fibers in the blended fabric.

### The Perfect Blend

With present-day processing machinery, it is impossible to obtain, for example, a blend of black and white fibers, in which the fibers are laid together in an orderly way so that black is always separated from black by white, and white is always separated from white by black. The best that can be obtained is a random distribution of single fiber elements in the three dimensions of the yarn. Although some products which fall short of this random distribution of single fiber elements are good enough for particular commercial purposes, it is probably true to say that all types of blending failure which do not involve long-period variations in the composition of the yarn are due to failures to obtain this breakdown of groups of fibers into single fiber elements, as is thought to occur sometimes in tow-to-top systems of processing where carding is omitted, or to regrouping of fibers of one kind during drafting. This may occur where there are gross differences between the staple lengths of the constituents of the blend, or when one fiber is very weak, so that a reduction in staple length occurs during carding. This second kind of failure, however, is always associated with a reduction in the regularity of the yarn.

It is usual to judge the intimacy of a blend by weaving yarns, dyeing the components different colors, and comparing the appearance of the fabrics. However, a more objective measure would be very useful, and clarity of thought would be improved if some sort of theoretical basis were obtainable. The counting of fibers in cross sections and construction of frequency histograms was shown by Lund [1] to be far less sensitive than the eye to differences in intimacy of blend, and it was suggested that a numerical assessment should be based on estimating in some way the size of the aggregates of one color in the blend.

Further thought and investigation has led to the application of the work of Spencer-Smith and Todd [4] and of Martindale [2] to this problem. They have shown, on a basis of random distribution of the fiber ends within the yarn, that the coefficient of variation of weight per unit length of the best yarns which can be produced on any present-day roller drafting mechanism is very nearly inversely proportional to the average number of fibers in the cross section of the yarn:

$$(CV)^2 = \frac{100^2}{n} + \frac{(CV_f)^2}{n}, \qquad (1)$$

* Presented before a meeting of the Textile Division, American Society for Quality Control, at North Carolina State College, School of Textiles, Raleigh, N. C., held on Feb. 4, 5, and 6, 1954.

where $CV$ = coefficient of variation of weight per unit length of the yarn, $n$ = the average number of fibers in a cross section of the yarn, and $CV_f$ = coefficient of variation of fiber weight per unit length.

Considering now only the lengthwise distribution of the fibers in the blend yarn, one may liken a 20s yarn of 50% black and 50% white fibers to two 40s yarns—one black and the other white—each yarn having a best regularity calculable from equation (1). Where one component may be dissolved out of the yarn by chemical means, the degree of regularity of the remaining component may be determined.

According to this concept,

$$(CV_A)^2 = \frac{100^2}{n_A} + \frac{(CV_{fA})^2}{n_A}, \qquad (2)$$

and

$$(CV_B)^2 = \frac{100^2}{n_A} + \frac{(CV_{fB})^2}{n_B}, \qquad (3)$$

where $CV_A$ and $CV_B$ are the coefficients of variation of the weight per unit length of fiber $A$ and fiber $B$ along the yarn, and $CV_{fA}$ and $CV_{fB}$ are the coefficients of variation of individual fiber weights per unit length of the two components. When considering man-made fibers, the two latter terms are quite small and may, for all practical purposes, be ignored.

Also, since, from the theory of analysis of variance,

$$CV^2 = (CV_A)^2 + (CV_B)^2 = 100^2\left(\frac{1}{n_A} + \frac{1}{n_B}\right), \qquad (4)$$

it is possible, knowing the coefficient of variation of the yarn within a given length and the coefficient of variation of fiber $A$ after dissolving out fiber $B$, to calculation the coefficient of variation of fiber $B$. It would also be possible to calculate a "quality number" [4] by relating the measured coefficient of variation to that of the most regular yarn theoretically obtainable according to equations (1), (2), and (3).

It is likely that the main importance of this line of thought is not so much the experimental techniques it makes possible, as the way in which it organizes observed phenomena into a coherent theory and makes it possible to predict the best possible appearance of a particular blend in a particular count.

Expressing equation (4) in another way, we have

$$(CV)^2 = 100^2\left(\frac{\text{equivalent cotton count } A \text{ as yarn}}{\text{cotton count fiber (fiber fineness) } A} + \frac{\text{equivalent cotton count } B \text{ as yarn}}{\text{cotton count fiber } B}\right). \qquad (5)$$

It follows from equation (5) that:

1. The higher the cotton count, the greater the irregularity; hence, when the yarns are spun from similarly proportioned blends of similar fibers, finer yarns appear less well blended than coarser yarns.

2. The lower the cotton count of the fiber, the greater the irregularity; hence, in yarns of the same count, those spun from coarser fibers will appear more streaky.

3. In a blended yarn, the variability of one constituent increases as its equivalent cotton count increases when the constituent is regarded as an independent yarn. Whence, in yarns of the same count, spun from blends of distinctly different colored fibers of the same size, those with distinctly unbalanced blends, such as 90/10, will appear more streaky than a 50/50 blend.

4. The irregularity of a constituent also increases with the coarseness of the fiber. From this, a good way to obtain a deliberately streaky effect is to use a small percentage of distinctly different colored fibers of a coarser denier than the rest of the blend.

All these phenomena occur in practice, indicating that the concept is at least sufficiently near to the truth to have a practical usefulness.

This concept does not explain the difference between a mock grandrelle yarn, a drawframe blend of similar fibers of the same color, and a carded or combed blend, but is nevertheless useful for application to blends where drafting in groups may take place due to differences in staple length, to gross differences in interfiber frictions, or to the omission of carding or combing after blending. This is, of course, the type of case where problems of this type normally arise.

Consideration along these lines of thought also makes it hard to visualize failure in "intimacy" of blending unaccompanied by a decrease in yarn regularity.

## Processing Factors and "Intimacy" of Blend

Fibers are not always blended in the picker room. They may be blended on a single-process lap-forming system: (*1*) before opening, (*2*) at the first or second head of drawing, (*3*) at the intermediate or roving frame, (*4*) at the creel of the spinning frame.

Although the card does not mix fibers completely at random—the streakiness of conventional card sliver from a blend of 50% black Coloray * and 50% white

* "Coloray" is Courtaulds' trade name for their brand of spun colored rayon staple fiber.

Fibro is evidence of this—it does at least break up the aggregates of fibers of one kind which occur in all blended laps.

A conventionalized diagram is given in Figure 1 of the type of cross section of a yarn containing 64 fibers in its cross section which may be expected from a 50/50 black and white blend of single fiber elements distributed completely at random. This was made by assigning a number from one of Fisher and Yates' tables of random numbers to each square, and blacking in each square to which second digits from 1–5 inclusive had been assigned.

Figure 2 represents a conventionalized mock grandrelle yarn, spun from one black roving and one white roving, the rovings having similar average weights per unit length. In this diagram the cross section was divided horizontally into two parts, and the assumption was made, for illustrative purposes, that randomization during drafting causes some transfer of black fiber to white roving and of white fiber to black roving. The chances for transfer were assumed to be 1 to 4. The blend is obviously less than ideally "intimate."

Figure 3 represents a blend at the last head of drawing, with eight ends up, spinning from double roving, giving drafting from sixteen elements of four fibers each to make a yarn. Since with units as small as this the element of chance in drafting must operate, the diagrammatic cross section of the yarn was divided into sixteen units of four fibers each. Each unit of four squares was given a digit from a table of random numbers, and those containing a second digit of 1–5 were given a 4 to 1 chance of being black, the remaining groups being given a 1 to 4 chance of being white. This blend is again less than ideally "intimate," but not so obviously far away as that illustrated in Figure 2.

When we try to make a similar conventionalized diagram of a blend made at the breaker drawing, we find that each yarn is being spun from elements of 128 card slivers ($8 \times 8 \times 2$). This is a larger number than the number of fibers in the cross section, and the conventional diagram to represent this must again be Figure 1, a random distribution of single fiber units.

We therefore arrive at the concept that when drafting of the different fibers takes place smoothly, a random arrangement of single fiber units should be obtained as soon as the number of doublings after blending exceeds the number of fibers in the cross section of the yarn, and that, considering blending only, finer yarns need fewer doublings to get random fiber arrangements. It is overwhelmingly clear that in finer counts as conventionally spun, there is no reason to worry about the "intimacy" of the blend.

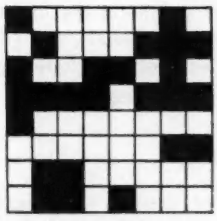

FIG. 1

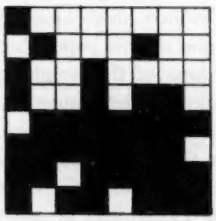

FIG. 2

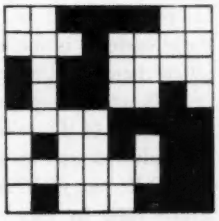

FIG. 3

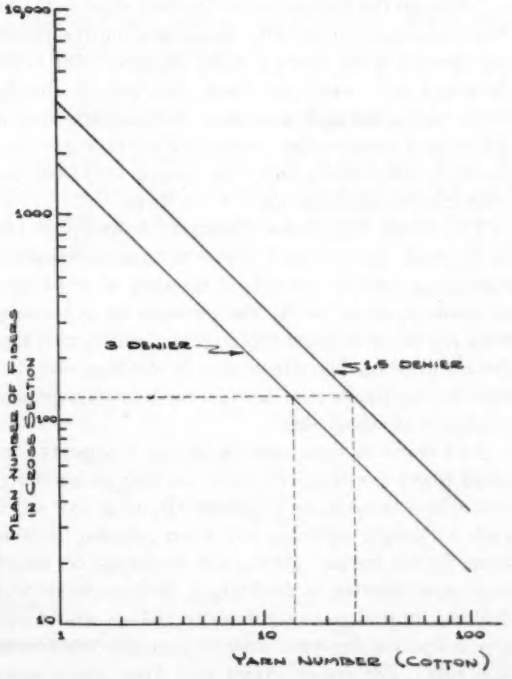


FIG. 4

The conventional process should ensure that the fibers are distributed at random across the yarn, provided that the doublings follow a carding or combing operation which does effectively break down groups of similarly colored fibers into single fiber drafting elements.

In Figure 4, the relationship between yarn number and average number of fibers in the cross section of yarns made from 3-denier and from 1½-denier material is shown. It is clear that the usual number of doublings after the card is sufficient to ensure random fiber arrangement in yarns down to 28$^s$ cotton count when spun from 1½-denier fiber, and down to 14$^s$ count when spun from 3-denier fiber.

This explains the experience of Lund [1], who, when investigating the suggestion made by Senior [3] that in order to obtain the best possible blend on the cotton system it is necessary to have a carded lap, carried out an experiment in three ways: (*1*) by carding on a flat card from a Derby Doubler prepared lap (double carding), (*2*) by carding on a flat card from a normal lap produced on a finisher picker, and (*3*) by carding on a Saco-Lowell three-roller and clearer card from laps produced on the finisher picker.

Although the appearance of the card slivers showed that there were great differences between the blending powers of the three carding systems, after three drawings (six ends up) and doubling at the fly frame and spinning frame there were no appreciable differences between the appearance of the yarns produced in these three ways, as judged by visual examination of knittings made from them.

The Wool Industries Research Association [5] in England reported that in one of their experiments comparing various methods of blending of wool tops, at some point in all of the methods of processing tried the fibers became thoroughly blended, and that the result of further attenuation by drafting was dictated merely by the statistics of a random arrangement of black and white fiber.

As a result of these considerations, it appears that when fibers are blended before carding or combing, and when breaker and finisher drawing are used, each with eight ends up, and when spinning is done from double roving, giving 128 doublings in all (a very usual number of doublings), then provided that drafting in groups does not occur (which would also give a less regular yarn than is normally considered desirable), 28$^s$ cotton count and finer yarns spun from 1½-denier fiber and 14$^s$ cotton and finer yarns spun from 3-denier fiber will always have a satisfactory degree of "intimacy," governed by the statistics of a random distribution of fibers.

According to these arguments, with fibers of similar staple length and frictional properties, there should be little difference between carded blends and drawframe blends in the finer counts, but, with 128 doublings in the system, the difference between the yarns produced by the two methods should become progressively greater as the yarn count decreases. When counts of the order of 6$^s$–9$^s$ are reached, one would expect a considerable difference between the two methods since yarns of this count are usually spun from single roving, giving only 64 doublings in the system.

It is apparent that when 3-denier fiber is being spun to counts of the order of 14$^s$–24$^s$, the degree of "intimacy" of blend in the lap is of no importance, but it is possible that gross differences in the size of aggregates of fibers of one kind or color in the lap would be detectable when 1½-denier fibers are being spun to coarse counts.

## Long-Term Variation in Composition

So far we have only discussed the "intimacy" of the fiber blend. A further problem of great importance is, of course, the maintenance of the correct proportions in the blend througout the whole program of spinning. The essential features necessary to obtain this are: (*1*) accurate weighing of the proportions of the raw materials used in the blends, (*2*) no very wide variations in the moisture contents of the constituents of the blends, and (*3*) an absence of selective action or "bunching" through the blending, opening, and picking range.

### *Accurate Weighing*

Many machine designs have been developed to give accurate proportioning of the raw materials, those in the U. S. by weighing and one in England by measurement of bulk. Detailed discussion of these systems is outside the scope of this paper, but all of them need adequate checking of the weighing or bulk-measuring device, at intervals determined by experience of the reliability of the individual system. It is always wise to check also that, for example, a 14,000-lb. run of 50% black Coloray and 50% white Fibro has, in fact, consumed 7,000 lbs. of each component.

*Variations in Moisture Content*

Variation in moisture content of the bales of raw material fed into the blend will cause some drift in the composition of the blend yarn being produced, but the effect is much smaller than has been supposed.

It is possible to show from first principles that

$$\frac{a}{a+b}\times 100 = \frac{100+y+\frac{C}{D}(100+y)}{100+y+\frac{C}{D}(100+y)+100+x+\frac{D}{C}(100+x)}, \quad (6)$$

where $a$ = the dry weight of component $A$, so that $a/(a+b) \times 100 = \%$ dry weight of component $A$ in yarn as tested, $b$ = the dry weight of component $B$, $x = \%$ moisture content in $a$, $y = \%$ moisture content in $b$, and $C/D$ = the blend proportion of a binary blend as weighed into the mixing, so that $C/(C+D) \times 100 = \%$ weight of component $A$ weighed into the blend.

From equation (6) a nomograph has been constructed, purely for illustrative purposes, to show the effect of variation in moisture content of the material fed into the blend on the oven-dry composition of a nominally 50/50 viscose/acetate blend yarn as tested.

Figure 5 shows a 50/50 viscose/acetate blend, with the viscose varying between 16% and 8% moisture content and the acetate varying between 10% and 2% moisture content. Taking the extreme variation from acetate with 2% moisture and viscose with 16% moisture, changing abruptly to acetate with 10% moisture and viscose with 8% moisture, no doublings in the system, the composition of the blend changes only from 46.8% viscose to 50.5% viscose.

It needs a simultaneous abrupt change of 4% in opposite directions in order to change the percentage viscose from 47.7% to 49.5%, and a simultaneous abrupt change of 2% in opposite directions changes the composition of the blend less than 1% of viscose or acetate.

Similar calculations on a 75/25 blend show that a simultaneous change of 4% in opposite directions changes the composition of the blend only from 73.2/26.8 to 74.6/25.4, a change of 1.4%.

It appears, therefore, that the normal small variations in moisture content of bales of fiber supplied by the producer are not likely to cause substantial variations in blend composition, particularly when a number of bales are used to feed the major portion of the blend, and particularly when the effect of doublings in the mill is considered.

*Absence of Selective Action in Blending, Opening, and Picking*

This may occur if the bulk densities, cohesions, or fiber sizes of the component parts of the blends differ greatly. It may occur in blending bins or in hoppers, and may usually be cured by putting deflector plates in blending bins and adjusting lattice speeds and comb settings in hoppers.

## Quality Control of Blends

The points in the production of blended yarns at which quality-control techniques may be applied are: (*1*) in the blending room, (*2*) at the finisher drawframe, and (*3*) on the yarn.

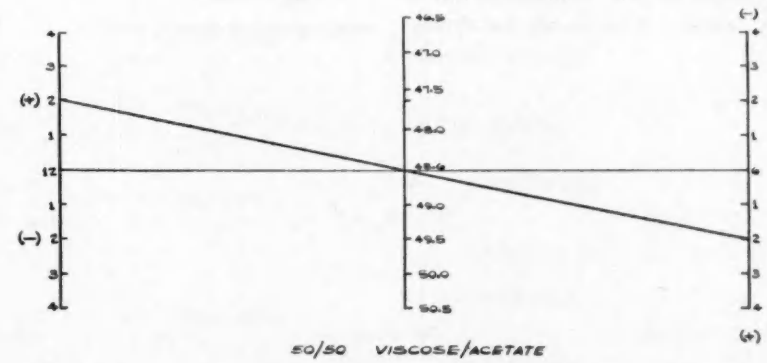


FIG. 5

(*1*) In the blending room, quality-control chart techniques may be used in checking the weighing mechanism of the blending feeder. In addition to this, of course, it is advisable to check the weights of fiber actually consumed in each blend. Although it is not necessary to check the moisture content of individual bales, any obviously wet bales should be set aside for invesigation, and not used in the mixing.

(*2*) Where blends of fibers which can easily be separated by chemical means are being processed, quality-control chart techniques may be used on the finisher drawframe sliver. This is sufficiently late in the process to be representative of the regularity of the product after most of the doublings, and sufficiently early for action to be taken if suspicious results are obtained. The best method is considered to be an analysis of a constant length of sliver. The results will have a variability due to the effect of the random distribution of fibers, but if the chart shows evidence of control, one can be confident that no drift in blend composition has taken place.

In the case of blends of similar fibers of different colors, such as blends of Coloray, quantitative measures are difficult, but color matching of finisher drawing sliver by eye, either under a North light or a Macbeth lamp, is very useful.

(*3*) It is very desirable to sample the spinning, and to either knit the samples in contiguous bands on a circular knitting machine or to weave them as filling in a filling-faced weave. Fibers which dye differently can then be differentially dyed, and the knittings or pieces of woven fabric examined, either under a North light or, preferably, a Macbeth lamp, for evidence of change in blend composition. This technique is particularly valuable in the case of blends of Coloray, where changes in blend composition can be seen immediately, without the necessity for dyeing.


## Summary

The work of Spencer-Smith and Todd and of Martindale has been applied to blend yarns, and it has been pointed out that: (*1*) finer yarns will appear less well blended than coarser yarns, when the yarns are spun from similarly proportioned blends of similar fibers; (*2*) in yarns of the same count, those spun from fibers of coarser denier will appear more streaky; (*3*) in yarns of the same count, spun from blends of distinctly different colored fibers of the same size, those with distinctly unbalanced blends, such as 90/10, will appear to be more streaky than a 50/50 blend; (*4*) streaky yarns may be produced by including a small proportion of distinctly different colored fibers of a coarser denier than the rest of the blend.

It is also reasoned that when drafting of the different fibers takes place smoothly, a random arrangement of single fiber units should be obtained as soon as the number of doublings after blending exceeds the number of fibers in the cross section of the yarn.

Results of calculations have been presented on the effect of variations in the moisture content of the raw material fed into the blend on the bone-dry composition of the yarn as tested, and the effects have been shown to be smaller than commonly supposed.


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# Nonionic Surfactants

## Their Chemistry and Textile Uses

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### Introduction

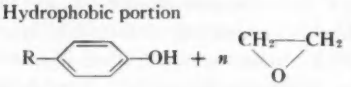
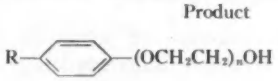
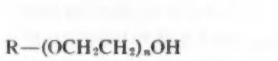
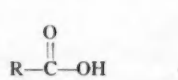
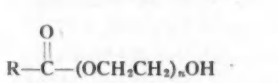
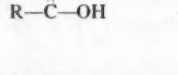
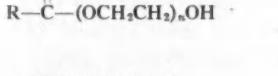
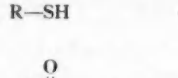
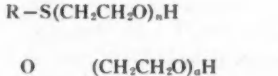
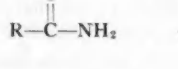
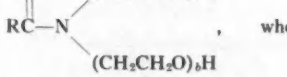
During the past decade, one of the most versatile and interesting classes of products which has attained widespread industrial usage is that of nonionic surface-active agents or surfactants. Since their first large-scale production and use in the United States in 1940 under the name "Igepal," * the production of nonionics in this country grew to over 70 million pounds in 1952 [21], and there are now many types available under numerous trade names. Although no figures are available, it is estimated that about 12 million pounds of nonionic surfactants were used in the textile industry in the United States in 1952. The largest quantity of these nonionic textile chemicals is prepared by the reaction of ethylene oxide with materials containing reactive hydrogen, such as alkylphenols, alcohols, acids, mercaptans, amides, and amines (see Table I). The polyoxyethylated amines, which exhibit cationic characteristics, especially in acidic media, are included because of their close structural relationship to the other ethylene oxide products.

Other types of nonionics which are similar to the ethylene oxide products are the fatty acid esters of sorbitan, which is a tetrahydroxy alcohol, or of sorbitol, a hexahydroxy alcohol. The water solubility of these products can be altered by causing them to react with various amounts of ethylene oxide. Since these sorbitan derivatives are esters, they are quite similar chemically to the polyoxyethylated acids.

New types of nonionics based on alcohols are the ethylene oxide derivatives of polypropylene glycol. Although propylene glycol itself is water-soluble, it

* Trade name of General Dyestuff Corp.

TABLE I. Preparation of Nonionic Surfactants from Ethylene Oxide

| Hydrophobic portion | | Product |
|---|---|---|
|  | |  |
| | |  |
|  | |  |
|  | |  |
|  | |  where $a + b = n$ |
|  | |  where $a + b = n$ |

has been found that when polypropylene glycol has a molecular weight higher than about 900, it becomes water-insoluble and can then serve as a hydrophobic base for nonionics [23].

The alkanolamine condensates of fatty acids are also surface-active in character. Since they are not used extensively in the textile industry, they will not be discussed in this paper.

It is obvious that it is possible to make an almost infinite number of nonionic surfactants, when one considers the number of long-chain alkylphenols, alcohols, acids, etc., which are available, and when it is realized that it is usually simple to vary *n*, the mole ratio of ethylene oxide to hydrophobic reactant, as desired. Thus, nonionics can usually be found for most applications where surface activity is required. Robinette [16] and Trinchieri [20] in recent years wrote general reviews on the various uses of nonionic surfactants in the textile industry. It is the purpose of the present paper to describe in greater detail how their physical properties, chemical properties, and performance characteristics are affected by changes in chemical structure, and what this variation of properties with structure means in terms of specific applications in the textile industry. Generalizations can be made which stress the strong points of the nonionics and at the same time point out their limitations for certain uses.

## General Nature of Surfactants

In general, surface-active agents are materials which, when dissolved in very low concentrations, lower the surface energy of the solvent to an extreme degree. For example, Igepal CO-630 * lowers the surface tension of water from 78 to 31 dynes/cm. when present at a concentration of only 0.01%.

Consideration of the phenomenon on the free surface of a pure liquid shows why small amounts of surfactants have such a profound effect on surface tension.

* Trade name of General Dyestuff Corp.

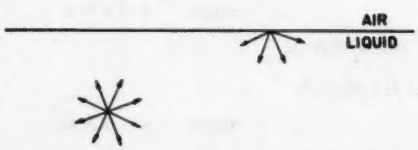



FIG. 1. *Molecular forces on the surface of a liquid.*

Figure 1 illustrates two molecules, one in the bulk of the liquid, subjected to the cohesive attraction of all its neighbors, and the other at the surface, subjected only to a one-sided attraction. It is evident that the uniform attractive pull on the former results in an equal attraction in all directions, so that the sum of all the force vectors is zero. On the other hand, the molecule located at the surface is subject to attractive forces only from the solution side; therefore, the pull on the surface is inward, so that the surface actually behaves as if it were compressed. The "state of compression" is illustrated by the experiment in which a dense object, such as a needle, is supported by the free surface of the water.

A quantitive measure for the peculiar surface condition of a liquid is the "surface tension," which is expressed in dynes/cm. or ergs/cm$^2$. It can be seen that this property has the dimensions of energy. For this reason, surface tension is sometimes referred to as "surface energy."

Figure 2 shows in detail the solution of a surfactant in water. For purposes of generalization, soap is depicted as the surfactant. The soap molecule consists of a hydrophobic portion—a long aliphatic hydrocarbon chain—attached to a polar portion, the negative carboxyl ion. The carboxyl ion, being strongly polar, is attracted to the polar $H_2O$ molecules, while the hydrocarbon chains of the molecules near the surface of the water tend to dissociate themselves from the water molecules. Thus, by their very nature, the surfactant molecules in a water solution tend to concentrate at the solution interfaces, so that their surface concentration is much higher than their bulk concentration. This behavior of surfactants is not limited to water-air interfaces.

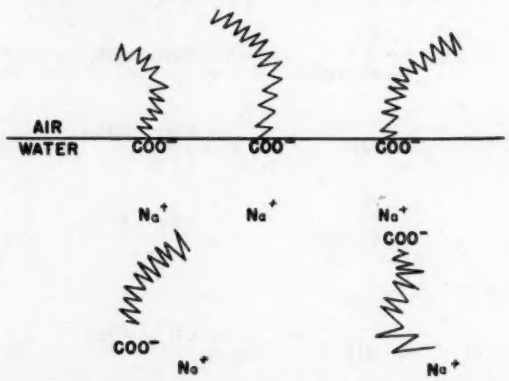



FIG. 2. *Orientation of soap at the air-water interface.*

Surfactants with the proper hydrophobic-hydrophilic balance may concentrate at many liquid-gas, liquid-liquid, or liquid-solid interfaces.

The effect of this surface concentration is given by important relationships developed by J. Willard Gibbs, which can be expressed in the following simplified form for dilute solutions:

*Gibbs adsorption isotherm:*

$$e = -c/RT\frac{ds}{dc},$$

where $e$ = excess concentration in the surface layer, $c$ = concentration in the solution, $S$ = surface or interfacial tension, $R$ = gas constant, and $T$ = temperature. Thus, the higher the concentration of the solute at the surface or interface, the greater the decrease of interfacial energy with respect to concentration.

As a surfactant is dissolved in a solvent, the surfactant molecules tend to concentrate at the air-liquid interface, which accounts for the profound effect of small amounts of a surfactant on surface and interfacial phenomena. This surface concentration continues as more surfactant is added, until a layer of surfactant, at most a few molecules thick, results. On further addition of the surfactant, the molecules dissolve in the bulk of the solution in clumps, or micelles. Thus, the typical surface-tension-concentration curve is obtained where the surface tension at first drops rapidly with respect to concentration, and then virtually levels off well before a concentration of 1% is reached. The concentration at which no further appreciable lowering of surface tension is obtained is known as the "critical micelle concentration."

## Mole Ratio Distribution and General Characteristics of Oxyethylated Products

The alkylphenol products are especially interesting for studying the variation of properties with structure. Their hydrophobe-hydrophile balance can be varied easily, either by changing the alkyl chain on the phenol or by using different mole ratios of ethylene oxide per mole of alkylphenol. Thus, it is easier to prepare a large variety of polyoxyethylated alkylphenols than of any of the other types of nonionics.

It has been recognized for years that a surfactant prepared from ethylene oxide is not a single compound, but is a mixture of closely related compounds possessing different mole ratios of ethylene oxide content to hydrophobic starting material.

Mayhew and Hyatt [12] have recently shown, in a study of the reaction products of nonylphenol with ethylene oxide, that the weight percent distribution of fractions containing the various moles of combined ethylene oxide follows Poisson's distribution formula. Flory [7] demonstrated the same fact with regard to the reaction product of ethylene glycol and 10 moles of ethylene oxide. Thus, it is obvious that the composition represented by the mole ratio of ethylene oxide to the other starting material is an average figure.

There are several important properties and general behavior characteristics of the nonionic surfactants which depend on the fact that they contain polymeric ethylene oxide chains.

### *Physical Form*

Because polyoxyethylated nonionic surfactants are mixtures of different products, they tend to be liquids. By reaction with enough moles of ethylene oxide, solids can be produced, but these are usually low-melting, waxy products.

### *Freedom from Impurities*

Aside from the small amount of catalyst in the product, the nonionics as prepared are 100% surfactant, in contradistinction to the anionics, which usually contain inorganic salts as impurities.

### *Cloud Point*

A phenomenon which is common to most commercial nonionics is that of "cloud point"—*i.e.*, as the temperature of a dilute aqueous solution is increased, the product is thrown out of solution. The temperature at which the clear solution changes to a cloudy one is known as the "cloud point" of the product. Cross has shown that the cloud point of an alkylphenol-ethylene oxide product remains virtually constant in the range from 0.5% to 10% of surfactant in water [5]. The cloud point has been attributed to the fact that association occurs between the ether linkages of the ethylene oxide chain and water to form a hydrate. On heating, this association is destroyed, and the product becomes sparingly soluble.

### *Solubility in Aqueous Solutions*

The solubility of nonionic surfactants in solutions of electrolytes also shows this same dependence on hydration. In general, nonionics can be thrown out

of solution by high concentrations of salts and bases, but not so readily by acids. The salts and bases probably break up the hydration of the ether oxygens, and thus insolubilize the nonionic. Acids, on the other hand, form oxonium compounds with the ether oxygens, and thus the nonionic stays in solution.

The generalization that salts throw nonionics out of solution must be made with reservations. Table II summarizes the results obtained in solubility studies conducted on the reaction product of nonylphenol with 10 moles of ethylene oxide in aqueous solutions of various inorganic salts.

It is of interest to note that the nonionic was extremely soluble in solutions of chlorides of di- or trivalent metals, but exhibited a low degree of solubility in solutions of sodium chloride and of all of the sulfates examined.

*Solubilization and Compatibility*

McBain and coworkers [13, 14, 15] and Lambert and Busse [9] showed that many surfactants solubilize dyes. This is a general surfactant phenomenon which depends on the fact that substances of low water solubility dissolve in the surfactant micelles and are thus protected from the water. However, anionic and cationic surfactants, because of the charge on their hydrophobic portions, are limited in the substances which they can solubilize. This is perhaps best illustrated by the fact that anionic and cationic surfactants precipitate each other:

$$R\text{—}SO_3^-Na^+ + R_4N^+Cl^- \rightarrow R\text{—}SO_3NR_4 \downarrow + Na^+ + Cl^-.$$

Thus, anionic surfactants cannot be used to solubilize cationic materials, and vice versa.

Since nonionics carry no charge, they are compatible with either anionic or cationic materials. As a matter of fact, Lambert showed that nonionic surfactants will even keep certain ratios of anionic and cationic substances in solution together [8].

TABLE II. SOLUBILITY BEHAVIOR OF 1% NONIONIC IN SALT SOLUTIONS

| | | Concentration of salt required to insolubilize nonionic | | |
|---|---|---|---|---|
| Nonionic | Salt | Conc. (%) | Salt | Conc. (%) |
| Nonylphenol + 10 EtO | $CaCl_2$ | >20 | NaCl | 10 |
| Nonylphenol + 10 EtO | $MgCl_2$ | >20 | $Na_2SO_4$ | 6 |
| Nonylphenol + 10 EtO | $FeCl_2$ | >20 | $MgSO_4$ | 5 |
| Nonylphenol + 10 EtO | $NiCl_2$ | >20 | $FeSO_4$ | 3 |
| Nonylphenol + 10 EtO | $FeCl_3$ | >20 | $NiSO_4$ | 7 |
| Nonylphenol + 10 EtO | $AlCl_3$ | >20 | $Al_2(SO_4)_3$ | 3.5 |

*Sorption and Substantivity*

Weatherburn and Bayley [24] and others reported on the sorption characteristics of surfactants on a variety of fibers, but not on their substantivity or their resistance to rinsing. In general, the cationic surfactants are the most strongly sorbed by the fibers, and the nonionics the least. The anionic materials occupy an intermediate position, except in the case of cotton, where they are sorbed to a slightly lesser degree than the nonionics. For applications such as wetting or detergency, a certain amount of adsorption is desired, but in most of these instances it is necessary to rinse the surfactant subsequently. Nonionics exhibit this low degree of substantivity with all types of fibers, probably because they have no ionic charges or groups capable of forming stable complexes with the various fibers.

*Stability*

Many types of nonionics, because of their chemical structure, are quite stable to acid hydrolysis, alkaline hydrolysis, oxidation, and heat.

The ethylene oxide products of fatty acids, being esters, are very susceptible to hydrolysis, and the amide products are hydrolyzed under severe conditions. The mercaptan products are prone to oxidation by hypochlorite or peroxides, and the amine-ethylene oxide products are probably unstable to bleach. The ethylene oxide products of alkylphenols or alcohols, however, are unaffected chemically by acids, alkalies, or oxidizing agents.

In regard to the ionic types of surfactants, the sulfonates are also very stable, while the sulfates are very susceptible to hydrolysis under acid conditions. The cationics are stable to hydrolysis, but are prone to attack by oxidizing agents and discoloration by heat.

## Influence of Side-Chains on Properties of Polyoxyethylated Alkylphenols

In order to determine the effect of the change of the hydrophobic portion of alkylphenol-derived nonionics, a large variety of products were prepared from different alkylphenols.

By preparing products with about the same cloud point—*i.e.*, hydrophobic-hydrophilic balance—it is

possible to pin-point this effect of the hydrophobic group. From this work, the following conclusions were reached:

(*1*) In the case of monosubstitution on the phenol ring, the R group must have between 7 and 10 carbon atoms for maximum efficiency with respect to wetting and detergency. If the R group has more than 12 carbon atoms, the products retain good emulsification properties, even though they have poorer wetting and detergency.

(*2*) With respect to disubstitution, each R group should have between 4 and 7 carbon atoms for maximum wetting and detergency. However, Cross and Enyeart [6] showed in cases where the two alkyl groups are of about the same length that products of superior emulsifying ability can be obtained if the sum of the carbon atoms in the two chains is higher than 14.

(*3*) A lesser amount of work was conducted with trisubstituted phenols. The ethylene oxide derivative of triisopropyl phenol, was a good wetting agent, but was somewhat poorer in detergency than the product from a $C_8$ or a $C_9$ phenol.

In summary, it is apparent that the structure of the alkylphenol is important in order to obtain the correct hydrophobic-hydrophilic balance. As long as this balance is obtained, the alkyl groups on the benzene ring can be varied quite widely to obtain products of all-around utility. The most interesting fact concerning alkylphenols not possessing this balance is that superior emulsifying agents can be obtained in the dialkylphenol series by using dialkylphenols containing longer alkyl chains.

### Influence of Ethylene Oxide Content on Properties of Polyoxyethylated Alkylphenols

Significant changes in properties can also be obtained by varying the ethylene oxide content of the molecule—*i.e.*, its hydrophilic character.

The important physical properties and performance characteristics were determined for a series of ethylene oxide products of nonylphenol. Most of the generalizations which can be made about these materials apply to products of other hydrophobic materials.

Figure 3 depicts the effect exerted on the surface tension of water by various polyoxyethylated nonylphenol products.

The products having lower mole ratios of ethylene oxide have greater surface activity—*i.e.*, they exert a greater lowering of the surface tension at a very low concentration. The maximum lowering is effected at a concentration between 0.001% and 0.01%, at which point (the critical micelle concentration) the surface tension is lowered to about 30 dynes/cm. As the products contain more and more ethylene oxide, this surface activity becomes less pronounced, until with products containing around 25 or 30 moles of ethylene oxide, the critical micelle concentration is between 0.01% and 0.1% and the surface tension is only lowered to about 40 dynes/cm.

Similar results are obtained with respect to the ability to lower the interfacial tension between water

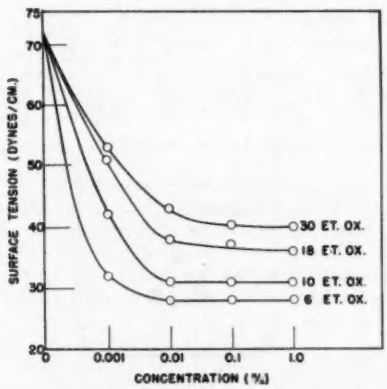



FIG. 3. *Surface tension at 25°C of aqueous solutions of nonylphenol-ethylene oxide products.*

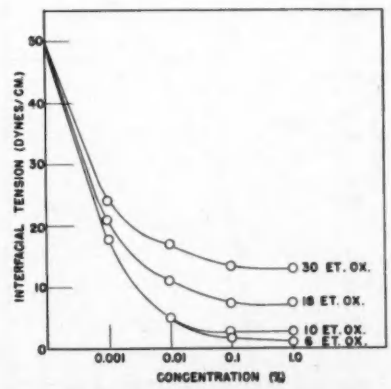



FIG. 4. *Interfacial tension at 25°C between aqueous solutions of nonylphenol-ethylene oxide products and Nujol.*

and a mineral oil such as Nujol (Figure 4). The 6- and 10-mole products have an appreciable effect on the interfacial tension between water and mineral oil. Thus, even though the 10-mole product is completely insoluble in mineral oil, it would be expected to be quite efficient in scouring hydrocarbons from surfaces.

As discussed previously, the cloud point is an important physical property of nonionic surfactants. Figure 5 shows how this varies with ethylene oxide content. As mentioned before, the cloud point of the nonionic depends on the hydrophilic character of the nonionic. Thus, the greater the ethylene oxide content of the product, the higher the cloud point, so that the nonylphenol products containing more than 15 or 16 moles of ethylene oxide are soluble in boiling water.

Closely allied with the cloud point of a nonionic is its solubility behavior in various solvents. Table III indicates the solubility of these nonylphenol products in two very different solvents.

In a hydrocarbon such as Stoddard solvent, the 4- and 6-mole ethylene oxide products are completely soluble, and the Stoddard solvent is appreciably soluble in the 10-mole product. In water, on the other hand, the 4- and 6-mole products are insoluble, while products with the higher mole ratios are completely soluble. The same pattern obtains with solvents not depicted in this table. None of these surfactants is soluble in mineral oil, although mineral oil does exhibit appreciable solubility in the 4-mole product. In a solvent such as butyl cellosolve, which possesses both polar and nonpolar properties, all of the nonionics in question are completely miscible in all proportions.

These results show why these surfactants are so versatile as emulsifiers. An emulsion may be defined briefly as a stable suspension of liquid particles within a second immiscible phase. In order to obtain this stable suspension, it is usually necessary to use an emulsifier. Figure 6 is a rough sketch depicting the mode of action of emulsifiers.

The nonpolar, alkylphenol portion dissolves in the water-insoluble droplet, while the polyoxyethylene chain dissolves in the water, thus stabilizing the emulsion. It is obvious how important solubility balance is in the case of emulsifiers. The surfactant must have exactly the right oil solubility and water solubility, or else it will be ineffective. With the nonylphenol-ethylene oxide series, it is possible to vary the solubility balance by varying the ethylene oxide content to obtain satisfactory emulsions in almost

TABLE III. SOLUBILITY BEHAVIOR* OF ETHYLENE OXIDE PRODUCTS OF NONYLPHENOL

| Moles of ethylene oxide | Stoddard solvent | | Water solvent | |
|---|---|---|---|---|
| | Surfactant in solvent | Solvent in surfactant | Surfactant in solvent | Solvent in surfactant |
| 4 | 100 | 100 | 0 | 0 |
| 6 | 100 | 100 | dispersible to 25% | 20 |
| 10 | 0 | 45 | 100 | 100 |
| 15 | 0 | 20 | 100 | 100 |
| 25 | 0 | 10 | 100 | 100 |

* Expressed as percent in solution at 25°C.

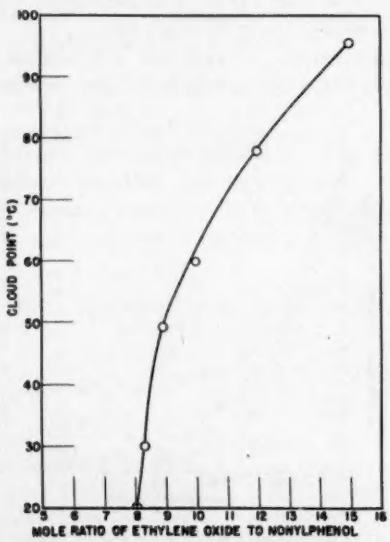
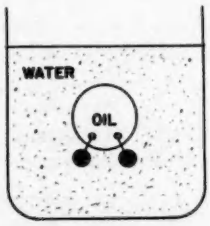



FIG. 5. *Cloud points of nonylphenol-ethylene oxide products in distilled water.*




● = WATER-SOLUBLE PORTION
○ = OIL-SOLUBLE PORTION

FIG. 6. *Sketch of oil-in-water emulsion.*

all systems. One exception is the case of self-emulsifiable mineral oil finishes, where the emulsifier must be soluble in mineral oil. None of the nonylphenol-ethylene oxide derivatives is satisfactory for this application, but a nonionic based on a longer-chain alkylphenol can be used.

Another type of material which is necessary to produce some emulsions is the so-called "coupling agent," which is used as a cosolvent for the emulsoid and emulsifying agent. Thus, a material such as the nonylphenol-10 mole ethylene oxide product, which is completely soluble in a polar solvent like water, and which also will dissolve 45% of a nonpolar material like Stoddard solvent, is very useful as a coupling agent, as well as an emulsifier.

An important property of surfactants is their ability to foam in aqueous solutions. The foaming ability of a series of nonylphenol-ethylene oxide products, as determined by the Ross-Miles test [17], is shown in Table IV. As the products become water-soluble, they produce more foam. Although no foam test is realistic for all conditions which may be encountered, this test gives a general indication of the tendency of a surfactant to form a stable foam. The alkylphenol-derived nonionics are intermediate in foaming tendencies in this test. For example, the foam heights obtained are appreciably lower than those for the high-foaming alkylaryl sulfonates, fatty-acid amidosulfonates, or alcohol sulfates, but are appreciably higher than those for low-foaming amidosulfonates or tall oil-ethylene oxide products.

One of the most important performance characteristics of surfactants in textile processing is that of wetting—that is, the ability to accelerate the penetration of aqueous solutions into yarns or fibers which have a water-repellent surface because of naturally occurring waxes or contaminants such as mineral oils.

Figure 7 depicts the results obtained in Draves wetting tests for a series of polyoxyethylated nonylphenols. The best wetting action is obtained with products having about 10–12 moles of ethylene oxide, and above this mole ratio, the products rapidly lose their wetting efficiency. Since irreproducible results were obtained with the lower mole ratio products in the 70°C wetting evaluation, the values are depicted by a dotted line. Although the mechanism of wetting action has not been completely elucidated, the wetting agent must hasten the penetration of aqueous solutions into the capillary interstices of the fibers or yarns. Thus, an agent which is too bulky in molecular structure decreases in its effectiveness as a wetting agent. This probably is one of the chief reasons why the polyoxyethylated products lose their wetting efficiency so rapidly after a certain mole ratio of ethylene oxide is reached.

An interesting fact, previously noted by Mayhew and Hyatt [12] and Wolfrom and Nuessle [26], is that nonionics can function effectively as wetting agents above their cloud points under the conditions employed in this test.

Another very important function which surfactants perform in certain textile operations is that of detergency. Reduced to its simplest terms, detergency or scouring is the removal from a surface of any material which is regarded as a contaminant. Although detergency can be defined in such simple terms, it is a complex operation involving many factors, such as adsorption, wetting, emulsification, suspending power, etc. For this reason, detergency evaluation involves the measurement of the removal of soil under conditions which approximate use conditions, and since detergency or scouring conditions vary considerably, depending on the opera-

TABLE IV. ROSS-MILES FOAM STABILITY OF SOLUTIONS* OF NONYLPHENOL-ETHYLENE OXIDE PRODUCTS

| Moles of ethylene oxide | Foam height (mm.) Immediate | After 5 min. |
|---|---|---|
| 5 | 15 | 12 |
| 6 | 28 | 18 |
| 10 | 70 | 58 |
| 12 | 102 | 90 |
| 18 | 114 | 97 |
| 30 | 106 | 86 |

* The aqueous solutions contained 0.05% surfactant.

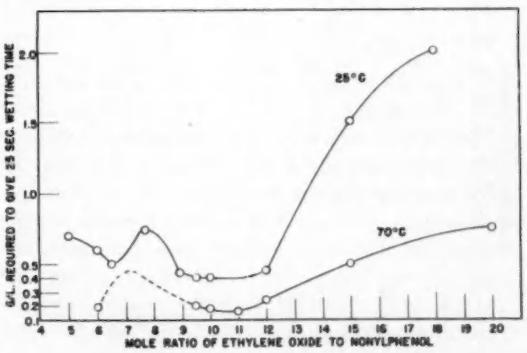



FIG. 7. *Wetting capacity of nonylphenol-ethylene oxide products in aqueous solutions at 25° and 70°C. Draves wetting test, 5 g. cotton skeins, 3 g. hook.*

tion involved, the results given below do not apply to every detergency application. However, they do give a good indication of the detergency which can be obtained with the polyoxyethylated nonylphenols.

Broadcloth swatches were soiled with a synthetic soil similar to hotel sweepings, described by Sanders and Lambert [18], to an initial reflectance of 30, using a magnesium oxide block as a reference of 100. The swatches were then washed in a Terg-O-Tometer, which roughly is a scaled-down agitator-type washing machine, in distilled water containing 0.25% of surfactant at 140°F for 15 min. After rinsing and drying, the reflectances were obtained. These results are shown in Figure 8.

The best results in these particular tests were obtained with a mole ratio of about 10. With the higher mole ratios, good but somewhat inferior detergency was still obtained.

As stated earlier, these tests were performed with a soil approximating hotel sweepings, which are similar to those encountered in the home. This soil is composed of approximately 90% solids and 10% oils and waxes. Lambert and Sanders [10] reported results obtained in cotton detergency with a polyoxyethylated alkylphenol on a different type of soil which is of interest to textile processing. This soil was a mixture of vegetable oil, mineral oil, and carbon black. With this oily type of soil on cotton, the polyoxyethylated nonylphenol alone was actually a better detergent than built soap, or two different built anionic formulations. These results are without significance with respect to household laundering, where the oily components are only a minor portion of the soil. However, many of the scouring and cleaning operations in the textile industry entail the removal of oils and fats, where emulsification and solubilization are more important factors. In such instances, as Lambert and Sanders have shown, the nonionics derived from alkylphenols are of particular value.

Figure 9 depicts results obtained in wool detergency tests where the wool swatches were soiled with a carbon tetrachloride suspension of carbon black, mineral oil, and vegetable oil to a reflectance of approximately 40. These swatches were washed manually at 39°C for 5 min. and then rinsed. This process was repeated, the swatches were dried, and the reflectances were determined.

In this case, where emulsification of oily impurities is of great importance, the products with a mole ratio of about 6–12 are the best, and the efficiency falls off rapidly as the mole ratio is increased about 15. It is of interest to note that the 6-mole ethylene oxide product gives good detergency results, even though the wash water is at a temperature above this surfactant's cloud point. Wolfrom and Nuessle [27] recently reported an instance where a nonionic is very effective for another detergency application under conditions above the surfactant's cloud point.

Another important performance characteristic of surfactants is that of lime-soap dispersion—that is, the efficiency of the surfactant in peptizing the hard-water soaps so that curds are not formed. This is not only of importance in uses where a surfactant is admixed with soap itself, but also where soap may be formed during processing by hydrolysis of fats and oils. In determining the lime-soap dispersing effi-

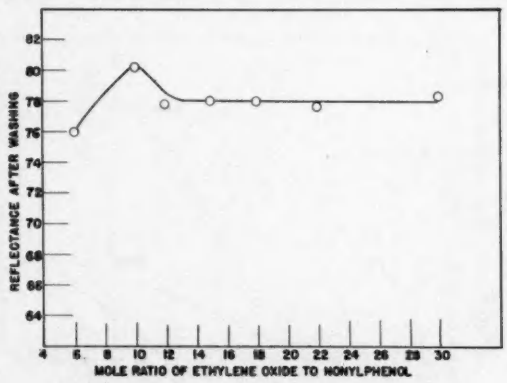



FIG. 8. *Cotton detergency of ethylene oxide products of nonylphenol; 0.2% detergent; initial reflectance of cloth, 30.*

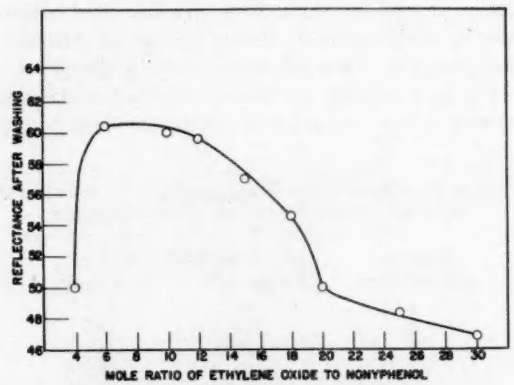



FIG. 9. *Wool detergency of ethylene oxide products of nonylphenol; 0.2% detergent; initial reflectance of cloth, approximately 40.*

ciency, the percentage of surfactant, based on weight of soap, which is necessary to prevent curd formation in excess hardness of water is determined according to the method of Borghetty and Bergmann [2].

This test is of necessity arbitrary, but it does give an excellent indication of the comparative efficiencies of surfactants for dispersing limesoap. Table V shows the results obtained with polyoxyethylated nonylphenols.

In this test, the lower the index, the better the material for lime-soap dispersion. Thus, the most efficient lime-soap dispersants are products having a mole ratio of about 10 and higher. Since this is a comparative test, the figures are not too significant by themselves. However, we have never examined a commercially available surfactant—nonionic, anionic, or catonic—which has a better lime-soap dispersion index than the polyoxyethylated nonylphenols.

To sum up this study of the influence of ethylene oxide content in polyoxyethylated nonylphenol products, the hydrophilic character, as expected, varies with the ethylene oxide content. Thus, products with lower mole ratios of ethylene oxide (3–6 moles) are more satisfactory in cases where a more hydrophobic surfactant is desired, such as hydrocarbon emulsification, while products with higher mole ratios (15–30) are more satisfactory in cases where a highly hydrophilic surfactant is required, such as processing in boiling water.

The most striking result of this work is the remarkable versatility of a product having the proper solubility balance, such as a product having about 10 moles of combined ethylene oxide. It is quite effective in lowering the interfacial tension between oil and water; even though it is completely miscible with water, it dissolves appreciable quantities of a hydrocarbon such as Stoddard solvent; it is a good all-around emulsifier, a highly efficient wetting agent, a superior cotton and wool detergent, and an outstanding lime-soap dispersant. Thus, for applications where a combination of performance characteristics, such as wetting, detergency, emulsification, or lime-soap dispersion, is desired, this type of product is of great utility.

TABLE V. LIME-SOAP DISPERSION INDICES OF ETHYLENE OXIDE PRODUCTS OF NONYLPHENOL

| Mole ratio of ethylene oxide | Lime-soap dispersion index* (%) |
|---|---|
| 6 | 10–15 |
| 10 | 4–6 |
| 12 | 4–6 |
| 18 | 4–6 |
| 22 | 4–6 |
| 30 | 4–6 |

* Percentage of surfactant, based on weight of soap, which prevents curd formation in excess hardness of water.

## General Performance Characteristics of Other Nonionics

With regard to ethylene oxide products of other hydrophobic materials, those prepared from straight-chain acids or alcohols give good detergents, but poor wetting agents [5]. In some cases, they are better emulsifiers than the alkylphenol products. Where the hydrophobic acid is not entirely straight-chain, such as tall oil, they are good cotton detergents, but are inferior in wetting and emulsification. The ethylene oxide products from branched-chain mercaptans are good all-around surfactants [5]. Where the hydrophobic group is polypropylene glycol, the products are poor wetters and emulsifiers, but can be built to give products with good cotton detergency.

If sorbitan or sorbitol is used as the water-solubilizing group, such as in sorbitol esters of fatty acids, very good water-in-oil emulsifiers are obtained. These esters may be rendered water-soluble by reaction with ethylene oxide to give good water-soluble emulsifiers, which are somewhat inferior in wetting.

## Uses of Nonionics in Textile Processing

After considering the influence of structure on the physical properties and general performance characteristics, it is of interest to note some of the more important applications of nonionic surfactants in textile operations.

### *Fiber Manufacture*

Excluding finishes, viscose rayon is the only fiber which utilizes surfactants during manufacture. The first step in the preparation of viscose is the steeping of wood pulp or cotton linters in approximately 18% caustic soda. If a solution of polyoxyethylated alkylphenol, which is stable in such a system, is sprayed on the crude cellulosic product before the steeping, it aids in the penetration of the caustic, even though it is insoluble in the caustic solution. The nonionic surfactant remains in the alkali cellulose produced in this operation, thereby reducing abrasion of the shredders, keeping them clean, and improving the filtration of the viscose after xanthation.

If delustering of the rayon is desired, it is usually carried out after the xanthation step by adding a dispersion of titanium dioxide, mineral oil, and sodium hydroxide. A combination mineral oil emulsifier and dispersant is required. It has been found that oil-soluble polyoxyethylated fatty acids are useful in this step.

An interesting application for nonionics has been found in the rayon spinning step, where the viscose solution is forced through spinnerets into a coagulation bath, which contains sulfuric acid, sodium sulfate, zinc sulfate, and sometimes glucose. During this operation, a sludge of sulfur, zinc sulfide, etc., is formed, which tends to form craters on the spinnerets, build up in the drain lines, clog the filters, and deposit on the spinning wheels and guides. A surfactant, to be of use, should be soluble and stable in this acidic system, disperse and soften the sludge, and adsorb on the metal spinnerets. Polyoxyethylated amides, because of the nitrogen in the molecule, adsorb on the platinum spinnerets to reduce cratering, and at the same time disperse the sludge sufficiently to prevent the sulfur from becoming tacky and the zinc sulfide from crusting so that they can be removed by filtration or other mechanical means.

*Fiber Finishes*

The manufacturers of man-made fibers usually apply a nondurable finish to provide lubrication, cohesiveness, antistatic properties, etc., during the subsequent carding, drawing, knitting, or twisting operations.

These finishing oils are very often formulations of different components, and vary for the different fibers. For this reason, only their general aspects are considered here. In many cases, the lubricant is mineral oil, while the antistatic agent may be either water-soluble or -insoluble. In these formulations, an emulsifier is required. Polyoxyethylated alkylphenols, alcohols, or fatty acids possessing short ethylene oxide chains are of value here, as are the sorbitol derivatives of fatty acids. Very often the antistatic agent may be incompatible with the mineral oil, and it is necessary to use a "coupling agent" or cosolvent. Since the alkylphenol derivatives containing 6–12 ethylene oxide units are soluble in, and also dissolve, a wide variety of polar and nonpolar materials, they have been found useful for this purpose.

In some cases the nonionics are better lubricants than mineral oil. The ethylene oxide products of fatty alcohols or acids are usually superior to similar products of alkylphenols, probably because the straight-chain or fatty character of the hydrophobic portions of the former materials have better lubricating properties than do the alkylphenoxy groups. Similarly, sorbitol derivatives of fatty acids may be of value as textile lubricants.

To sum up this discussion of finishing oils, the nonionics are of particular value because of the wide variations possible in the hydrophobic portion, the ease with which their hydrophilic character can be altered, the absence of inorganic salts or water as impurities, and their compatibility with cationic and anionic materials.

*Raw Wool Scouring*

All shorn wool must be scoured to remove dirt, sand, suint, and grease. In this process, raw wool loses 25%–50% of its weight. Borghetty [1] reported on the effective use of soda ash along with a nonionic surfactant. The soda ash is used to saponify as much of the grease as possible, while the surfactant serves as an emulsifier, detergent, lime-soap dispersant, and suspending agent. Since the alkylphenol-derived nonionic detergents are particularly outstanding for removal of oily types of soils and for lime-soap dispersion, they have been widely used for wool scouring. Anionics, such as the alkylaryl sulfonates, have also been used, but they suffer from their substantivity to the wool, which necessitates more frequent replenishment of the bath. Nonionic surfactants derived from tall oil and from tertiary dodecylmercaptan are also employed. The tall oil product, however, is only about 70% as efficient as the alkylphenol-derived scouring agent when evaluated by the A.A.T.C.C. method [19], probably because of its poorer wetting, emulsifying, and lime-soap dispersing powers. The mercaptan product is as efficient as the alkylphenol product, but if it is not completely rinsed from the wool during the scouring operation, it will impart an odor to the wool in subsequent carbonizing and bleaching operations.

*Carbonizing*

Scoured wool stock or woven piece goods are treated with an acidic material such as sulfuric acid or aluminum chloride to embrittle cellulosic materials, burrs, etc., so that they can be removed by dusting. A surfactant is needed to emulsify residual grease and oil as well as waxy surfaces of the burrs and to in-

sure complete and uniform wetting of the material. In addition, it must be stable to the acid in the subsequent baking operation. The alkylphenol-ethylene oxide derivatives possess the desired properties for the processing step. However, when piece goods are carbonized "in the grease," these nonionics are too efficient, since the amount of grease and oil emulsified contaminates the impregnating bath. In such case, an acid-stable anionic wetting agent which is a poor emulsifier is preferable.

*Desizing*

For desizing cotton, a good wetting agent is required which is low-foaming, stable to heat, noninjurious to enzymes, and stable to cold dilute acid. The same criteria apply to desizing assistants for other fibers sized with starch. The nonionics based on alkylphenols have the requisite wetting power and stability, and in addition do not have an adverse effect on enzymes. For these reasons they are used extensively in this operation. With the tendency towards higher-speed padding of piece goods with enzyme solutions, these nonionics tend to give too much foam; so there is a need for a lower-foaming, high-wetting nonionic.

The alkylphenol-derived nonionics are also used for assisting in desizing man-made fibers which are sized with gelatin or synthetic polymers. In such cases, the surfactant is used for its detergent properties rather than for its wetting properties.

*Bleaching*

In bleaching by peroxide or hypochlorite, surfactants are used to aid in penetration and in the removal of surface impurities such as pectins, waxes, or oils. They must of necessity be stable to oxidizing agents under alkaline conditions. Consequently, the alkylphenol products are preferable to those derived from mercaptans or acids. In the high-speed continuous bleaching operations, the high rate of solubility, quick rinsability, and high suspending power of the nonionics make them particularly advantageous.

*Scouring before Dyeing*

In general, all types of fibers must be scoured before bleaching and dyeing. In the case of cotton, builders such as soda ash or caustic soda are used in conjunction with the surfactant to remove natural waxes, suspend solid materials, and disperse hard-water soaps resulting from saponification of the waxes. With wool, the chief impurities to be removed are residual wool grease, lubricants, and hard-water soaps if the scouring is done after an alkaline fulling process. Thus, with either fiber, a good all-around detergent emulsifier, and lime-soap dispersant is required, and for this reason the alkylphenol products containing 8–12 moles of ethylene oxide have been widely used. In the case of cotton, anionics such as the alkylaryl sulfonates and fatty-acid amidosulfonates are also employed. With the tendency towards higher-speed processing, however, the nonionics are coming into greater use because of their higher rate of solubility and their quick rinsability. If a softer hand is desired, the amidosulfonates are preferable.

Wool in some cases contains relatively large percentages (over 3%) of oil and grease. This is especially true after garnetting, where larger quantities of fiber lubricants are required. The best scouring results are obtained by using a dilute acetic acid scouring solution in which a reaction product of an alcohol with 15–30 moles of ethylene oxide is used as the scouring agent.

*Dyeing and Printing*

In dyeing and printing, surfactants are used chiefly for wetting and levelling. Levelling agents are needed particularly where the dyes have too great an affinity for the fiber in relation to their rate of diffusion into the fiber, and therefore do not dye the fiber at a uniform rate. Valko [22] showed that nonionic levelling agents, by combination with the dye ions, cause an increase in the particle size of the dye, thus retarding the dyeing action. However, since the dye has a higher affinity for the fiber than for the surfactant, it slowly exhausts on the fiber, thus giving an even dyeing.

Brauer [4] postulated that the nonionic levelling agent forms an oxonium ion with the dye. Whether an actual oxonium compound is formed or whether the dye is dissolved in the surfactant micelle with the formation of a looser complex has not been demonstrated, but the free electron pairs on the ether oxygens very likely are responsible for the levelling action of the nonionics. Products of a higher mole ratio of ethylene oxide (15–30) with alcohols have proved to be particularly effective, because the greater number of ether linkages provides for greater opportunity for solubilization or complex formation, and

because a higher cloud point product is needed at the elevated temperatures used in many dyeing processes. Since there are no ester or sulfide linkages in these surfactants, they are stable in the presence of salts, acids, or alkalies which may be employed.

These same nonionics derived from alcohols may serve a variety of functions in naphthol dyeing. Because of their complexing ability, they aid in dissolving the fast-color salts and exert a favorable influence upon the stability of the diazonium compound in solution. Furthermore, in the coupling bath, the surfactant disperses the pigment which is formed. Thus, the fabric can readily be rinsed, and an improvement in crockfastness is obtained.

In many cases, these nonionic levelling and dispersing agents are sufficiently good wetting agents to provide the necessary wetting and penetrating. If a stronger penetrant is desired, the alkylphenol derivatives can be used to advantage alone or in conjunction with the levelling agent.

Closely allied with levelling action is that of stripping. Dyed fabrics are stripped to change shade, improve uniformity, or permit reuse of dyed material. The same nonionic surfactants which are used for levelling may be used for stripping. However, the nonionics may not have a strong enough solubilizing action on the dyes where stripping is the primary goal and levelling is not required. In such cases, a weakly cationic polymer, such as polyvinylpyrrolidone, has proved to be preferable to the nonionic surfactants because of its greater affinity for many dyes [4].

*Scouring after Dyeing*

Dyed or printed goods are usually scoured to remove loose color, to remove mineral oil after the Williams hot-oil, continuous-dyeing process [25], or to develop shade (oxidize). These operations require an agent with good all-around detergent, dispersive, emulsifying, and rinsing properties. Where perborates or chrome-acetic acid are used to develop shade, stability to oxidizing agents is required. Thus, the ethylene oxide products of alkylphenols are of great utility in this step. Anionics with all-around surfactant properties, such as the alkylaryl sulfonates or the amidosulfonates, are also effective. For certain operations, the nonionics hold definite advantages. Where there is not much agitation, the high speed of solution of the liquid nonionics is advantageous, as is their quick rinsability. It should be mentioned that this rinsability is a disadvantage in cases where a soft hand is desired. Fat-derived anionic surfactants, such as the amidosulfonates, are preferred in such cases.

*Fabric Finishing*

The nonionic surfactants are not used as durable finishes because of their nonsubstantivity. They are, however, of particular interest as penetrants because of their compatibility with either anionic or cationic finishing agents. For example, Borghetty, Pardey, and Sherburne [3] reported that the nonionics obtained by the reaction of 8–12 moles of ethylene oxide with alkylphenols aided greatly in the application of the phosphonium chloride type of mothproofing agent to wool. This nonionic maintained an excellent suspension and emulsion of the contaminants, aided in penetration, and was compatible with the quaternary agent.

One of the problems which is common to fabrics made of synthetic fibers is that of static generation. The need for a durable antistatic agent which is fast to multiple washing and dry-cleaning operations is great, but so far a satisfactory material of this type has not been developed. Another solution of the problem is the use at the mills of a material in a final rinse which would have sufficiently good storage properties to remain effective on the fabric until it is used by the consumer. If this same antistatic agent is a good fine-fabrics detergent, it can be used by the housewife in the rinse to impart antistatic properties to the fabric each time it is washed.

The data given in Table VI indicate that such an approach is feasible. Swatches of various fabrics were

TABLE VI. ANTISTATIC ACTION OF REACTION PRODUCT OF NONYLPHENOL WITH 10 MOLES OF ETHYLENE OXIDE

| | Charge developed (units of $2.7\times10^{-10}$ coulombs*) | | | | |
|---|---|---|---|---|---|
| | | Rinsed, 1% solution of agent | | Rinsed, 0.25% solution of agent | |
| Fabric | No agent | 1 wk. storage | 9 wks. storage | 1 wk. storage | 9 wks. storage |
| Dacron | 500 | 12 | 15 | 18 | 30 |
| Orlon | 500 | 24 | 30 | 84 | 100 |
| Nylon | 400 | 15 | 70 | 72 | 150 |
| Acetate | 600 | 18 | 90 | 60 | 120 |
| Dynel | 550 | 27 | 30 | 48 | 130 |
| Acrilan | 500 | 18 | 45 | 30 | 80 |
| X-51 | 650 | 48 | 48 | 96 | 195 |

* Determined at 40% R.H. and 80°F.

rinsed in solutions of polyoxyethylated nonylphenol and allowed to dry. Electrostatic generation was measured at 80°F and 40% relative humidity in an apparatus which is a modification of that described by Lehmicke [11].

The results obtained show that this product is effective in reducing the charge generated on a wide variety of synthetic materials. Other experiments have shown that, in general, the same synthetic fabrics treated with this agent possess a conductivity equivalent to that of cotton.

Even though this agent exhibits all-around antistatic action, it is not a cure-all. With respect to a final rinse in mill processing, these data are a general indication of what can be accomplished. For each specific fiber, a better agent might be found than the one used in these tests.

For household washing, however, an agent is required which is effective on a variety of fabrics. The surfactant used in these tests is a very efficient fine-fabrics detergent. If it is used in the rinse water in a concentration of 0.1%–0.2%, it will alleviate many of the static problems encountered in consumer usage.

## Conclusions

In summary, the following general advantages of nonionics for textile applications are apparent: (*1*) Their liquid form and lack of substantivity fit them particularly for modern high-speed processing where ease and speed of solution and speed of rinsing are required. (*2*) Their compatibility with a wide variety of materials makes their use possible in many types of formulations. (*3*) The alkylphenol derivatives possessing the proper hydrophobic-hydrophilic balance are of particular value for many operations, because of their good wetting, emulsifying, detergent, and lime-soap dispersing properties, coupled with their stability to acid, alkali, and oxidizing agents. (*4*) When a surfactant with a specific property is required, a "tailor-made" nonionic can very often be developed because of the wide variety of hydrophobic materials which can be used and the ease with which the polar character of the surfactant can be varied by using more or less ethylene oxide in its production.

As to their limitations, the following are worthy of note: (*1*) The most versatile nonionics are sparingly soluble in hot aqueous solutions (above 70°–80°C) and in many concentrated solutions of electrolytes. (*2*) Because of their quick rinsing and lack of substantivity, the alkylphenol-derived nonionics have no softening effect on the fabrics. (*3*) In some cases where low foam is required, the nonionics foam too much. In other cases where high foam stability is required, the nonionics do not foam enough. This latter requirement is of much more importance in the household than in industry.

What are the major developments in prospect for the nonionics?

In regards to the development of a versatile all-around nonionic which is soluble in boiling water and in concentrated electrolyte solutions, the prospects are dim. Studies to date with the different hydrophobic types have always given the same result: As soon as the nonionic is rendered sufficiently water-soluble to have a cloud point of about 100°C, it no longer possesses good wetting and emulsifying properties. This goal may eventually be reached, but it probably will require a radically new approach.

The same may be said for the development of a quick-rinsing, nonsubstantive nonionic which will leave as soft a hand as do such anionics as the amidosulfonates. If we demand an almost completely rinsing surfactant, in all probability we shall have to expect little or no softening action.

Brighter prospects are in store for improving the foaming characteristics of nonionics. The ethylene oxide reaction products of tall oil and also of polypropylene glycol are very low-foaming, but lack good all-around surfactant properties. However, it is probably only a matter of time until a versatile nonionic surfactant is developed which will possess the low-foaming properties required in processes employing high agitation.

With respect to the development of a nonionic which will give foam as stable as some of the anionics, this may be termed one of the classical unsolved problems of the surfactant industry. The fact that the various manufacturers of nonionics have investigated this problem for years and have not yet found a solution is sufficient indication of its complexity and difficulty. Nevertheless, this problem also will probably be solved as additional fundamental information is obtained concerning the nature of foam.

Passing from the scientific to the economic sphere, it would be well to speculate for a moment on the economic future of the nonionics. The alkylbenzene sulfonates, like the nonionics based on alkylphenols, are versatile surfactants. However, the sulfonates are truly mass-production chemicals, and in many cases have been used instead of the nonionics because

of their lower cost. As the nonionics achieve larger-volume production, it is logical to assume that their prices will fall in relation to the sulfonates, which have already attained large-volume production.

Consequently, it is safe to predict from both the scientific and economic viewpoints that during the next five years the nonionic surfactants will be used to a proportionately greater extent in the textile industry than they are today.

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# The Improvement of Luster of Cotton

## Part IX: Thermosetting Resins*

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**Abstract**

The range of increase of luster from the application of thermosetting resins in a cotton twill is found to be as large as that produced by mercerization and to be generally similar in appearance. Further increases in luster, as measured by contrast ratio, can be obtained by high pressure embossing, although the appearance of the embossed areas is different and can be recognized as flattened.

Various types of urea formaldehyde and melamine formaldehyde resins are very similar in their effects on the luster of cloth, and variations in mechanical smoothing similar to tentering or light calendering have more influence on luster than the type of resin. The resins do differ, however, in their effect on wrinkle recovery, stiffness, and tensile and tear strength.

Thus it appears that the chief effect of thermosetting resins on luster of fabrics is indirect, through their durable control of fabric structure. The direct effect of the resins on luster, as shown by tests on yarns, is to decrease the luster of mercerized cotton and only slightly to increase the luster of nonmercerized cotton.

### Introduction

The improvement of luster of cotton fabrics by treatment with thermosetting resins is usually a by-product of other effects desired from these finishes, such as wrinkle resistance and recovery, crispness, clearness of surface or control of fuzz, and dimensional stability. In other cases the resin is used to hold the fabric in embossed forms or to increase the durability of friction or Schreiner finishes. The fabric may even become a carrier for a flexible film of resin and other material which may be itself glazed or embossed with a pattern. Thus the effects of thermosetting resins on luster may be examined in terms of effects arising directly from the resins, or of effects arising indirectly through changes of fabric structure which can be made durable by the resins.

The direct effect of the resins is obvious when a film, compounded mainly of resin, replaces the original fabric surface. However, the luster of such a film or the contrast of different directions in the film depends more on the smoothness of glazing or the embossing pattern than on either the cotton fabric base or the nature of the resin. There is a possibility of direct effects of resin in finishes in which there is no general film through local sparkle from small areas of film on yarn surfaces or fibers. However, the indirect effects, through durable control of cloth structure, appear to be at least as important as the choice of resins, if not more so, as far as luster is concerned.

Typical commercial thermosetting resins based on urea formaldehyde, melamine formaldehyde, and modifications of these have been used in this work. While there may be differences in effect on luster between types of resins and between resins from individual sources, the present work is not regarded as demonstrating such differences, but rather, as indicating general similarity.

One question involved in that of type of resin, aside from constitution of the monomer, is the degree of polymerization at the time of application, since this governs the extent to which the resin can diffuse into the fibers, or must be deposited as a surface film on the fibers [9]. In most of the present work the effort has been to secure monomer diffusion and polymerization within the fiber to the extent usual in commercial practice. However, some attempts to increase the on-fiber and decrease the in-fiber deposition have been included for comparison.

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### Effects of Resins on Yarns

In an effort to get away from the complications of fabric structure, and examine the direct effect of the resins themselves, skeins of yarn have been treated with resins in a manner parallel to the treatment of fabrics, using the same resin-treatment solutions. The skeins underwent squeezing through rolls to control wet pickup, and were dried and cured under the same conditions of time and temperature as the fabrics. After curing, the skeins were washed by hand and let dry slack. The yarn was then wound on cards for measurement of contrast ratio [8].

Even with yarns, one indirect or structure control effect, an effect on yarn straightness, can be recognized. Table I compares skeins which were allowed to hang slack during the drying and curing of the resin, with skeins which were held taut, at 102% of original length, during these stages. Both sets were dried slack after washing to remove excess resin and soluble materials. The luster of yarn from taut skeins is often considerably increased above that of the slack skeins. This, and the appearance of the yarns, suggests that the difference is one of structure control, in the taut case the resin helping to hold the yarn straight, and in the slack case, tending to set the irregularities of direction.

*Comparison of Resins*

Table II shows a series of laboratory prepared or commercial resins applied to both mercerized and kiered cotton yarn, all held taut during the resin drying and curing. Each commercial resin was made up with catalyst and softener or wetting agent, according to the directions of the supplier. The urea formaldehyde resins were varied in molecular ratio of urea to formaldehyde. For the 1:2 ratio, commercial dimethylol urea was used; for the other ratios, urea and formaldehyde were combined according to procedures recommended for textile finishing [10].

In every case, the luster of mercerized yarn is lowered, while for the yarn which was kiered only, the same resin treatments increased the luster. The mercerized yarns after any of the resin treatments will still be recognized as high luster, mercerized yarn, while none of the increases on yarn which has been kiered but not mercerized bring this into the mercerized range. The range of lusters for the various resin types is generally the same.

The lowering of luster of mercerized yarns suggests that surface deposits of resin on smooth fibers may be increasing the scattering of light. This is borne out by trials on bright filament rayon yarn. The contrast ratio for untreated yarn was 136; for yarn with 10% add-on of melamine resin MFB, applied to taut skeins, the contrast ratio was reduced to 50. The luster of filament rayon lining twill was also reduced by applying resins.

The increase of luster for the kiered yarn is a change for which it is more difficult to offer an explanation. The increase for the kiered yarn is smaller than the decrease for the mercerized yarn. Two factors which may be involved are possible laying of fuzz on yarn surfaces, cementing free fibers

TABLE I. STRUCTURE EFFECTS IN YARN SHOWING CHANGE PRODUCED BY DRYING THE RESIN SOLUTION ON TAUT SKEINS AT 102% STRETCH, IN CONTRAST TO SLACK SKEINS *

| | Luster (contrast ratio) | | | |
|---|---|---|---|---|
| | Mercerized | | Kiered | |
| Resin | Slack skeins | Change with taut skeins | Slack skeins | Change with taut skeins |
| Urea formaldehyde | | | | |
| 15% UF 1:2 | 2.34 | 0.00 | 1.54 | 0.09 |
| 12% UF 1:2 | 2.29 | 0.10 | 1.50 | 0.07 |
| Melamine formaldehyde | | | | |
| 15% MFA | 2.65 | −0.01 | 1.63 | 0.01 |
| 15% MFC | 2.65 | 0.13 | 1.64 | 0.03 |

* The yarn was 60/2 cotton, commercially spun and mercerized, and the corresponding commercial natural yarn, kiered in the laboratory.

TABLE II. VARIOUS RESINS ON 60/2 COTTON YARN, DRIED AND CURED UNDER TENSION

| | Luster (contrast ratio) | |
|---|---|---|
| Resin | Mercerized | Kiered |
| None | 2.98 | 1.61 |
| Urea formaldehyde | | |
| 10% UF 1:1 | 2.75 | 1.66 |
| 10% UF 1:1.6 | 2.82 | 1.69 |
| 15% UF 1:2 | 2.34 | 1.63 |
| Modified urea formaldehyde | | |
| 10% UFMA | 2.73 | 1.67 |
| 10% UFMB | 2.65 | 1.69 |
| Melamine formaldehyde | | |
| 15% MFA | 2.64 | 1.64 |
| 10% MFB | 2.64 | 1.69 |
| 15% MFC | 2.78 | 1.67 |
| Mixture | | |
| 10% UFA (4.4%) + MFB (5.6%) | 2.69 | 1.68 |

to the yarns, and local formation of surface films of resin. There is also a possible small swelling of the flat convoluted cotton hairs, which might be "set" by the resin—that is, an effect like the swelling of mercerizing, but on a very reduced scale. The most significant point is the small extent of the change in nonmercerized yarns.

## Effects on Fabric

### *Amount and Type of Resin*

One fabric, a white cotton twill, was used for all the experiments on fabric reported in the tables.* Table III shows the effect of several resins at three levels of add-on; Table IV shows several other resins at 10% add-on. These tables also compare variations in mechanical treatment of the fabric during the drying of the resin, which have effects on cloth structure which will be discussed later. For the present point, the effect of either amount or type of resin, comparison within any one type of mechanical treatment indicates that the different resins are very similar in effect on luster, and that the effect of amount of resin is small, in the range from 5% to 15%, although there is a small trend for more luster with more resin.

The general procedure for fabric treatment was to make up the resin solution to give the required add-on of resin solids for 60% wet pickup. Fabric specimens were marked before treatment, so that the wet fabric could be stretched 5% in each direction on a pin frame for drying. All fabric specimens in Tables III and IV were stretched in this way on pin frames, and dried at 190°F for varying lengths of time, depending on the mechanical treatment involved. After further mechanical treatment in the course of which the drying is completed, or after complete drying on the pin frames, the resin was cured at 300°F for 3 min. After curing, the samples were washed in a Bendix automatic washer to remove any excess resin. After the initial washing, additional washings were given certain samples to test the durability of the resin.

The washed fabrics were all put in a uniform condition for measurement of luster by drying in a flat bed press, using a press cloth over the face of the fabric.

### *Comparison of Yarns and Fabrics*

In spite of the complications of cloth structure, the increase of luster on nonmercerized cloth is usually considerably larger than that observed on nonmercerized yarns. Part of this increase of luster may be due to the fact that the fabrics were measured for luster in single layers, while the yarns were examined in windings seven layers deep, with total cover factor over 100. It has been shown [7] that increased scattering from deep layers reduces the contrast ratio, and this also reduces the range of change in contrast ratio, which puts the measurements on yarns at

* Cloth, cotton drill, 7 oz., white. 2/1 Twill, 35 in. 78 × 48, carded. JAN Specification C300.

TABLE III. Effect of Various Add-ons on Luster of Cotton Twill Contrast Ratio of Untreated Control 1.25

| Add-on (%) | Resin | Luster (contrast ratio) for mechanical treatment: Dried-on | Completely dried, ironed | Partly dried, ironed |
|---|---|---|---|---|
| 5 | UFA | 1.36 | 1.40 | 1.41 |
| 10 | | 1.40 | 1.42 | 1.43 |
| 15 | | 1.41 | 1.44 | 1.45 |
| 5 | MFA | 1.35 | 1.38 | 1.40 |
| 10 | | 1.35 | 1.40 | 1.43 |
| 15 | | 1.35 | 1.40 | 1.43 |
| 5 | MFC | 1.36 | 1.36 | 1.38 |
| 10 | | 1.37 | 1.38 | 1.39 |
| 15 | | 1.36 | 1.40 | 1.42 |

TABLE IV. Drying Conditions and Low Pressure Mechanical Smoothing, for 10% Add-on of Various Resins on Cotton Twill, Contrast Ratio as Received 1.25

| Resin | Washings | Luster (contrast ratio) for mechanical treatment: Dried-on | Partly dried, ironed | Damp ironed |
|---|---|---|---|---|
| UF 1:1.6 | 1 | 1.37 | 1.40 | 1.42 |
| | 5 | 1.33 | — | 1.34 |
| UFMA | 1 | 1.36 | 1.39 | 1.38 |
| | 5 | 1.34 | — | 1.35 |
| UFA 4.4% + MFB 5.6% | 1 | 1.29 | 1.36 | 1.35 |
| | 5 | 1.30 | — | 1.32 |
| UFMB | 1 | 1.35 | 1.38 | 1.38 |
| | 5 | 1.32 | — | 1.35 |
| MFB | 1 | 1.31 | 1.37 | 1.36 |
| | 5 | 1.29 | — | 1.33 |
| MFC acid colloid | 1 | 1.31 | 1.36 | — |

TABLE V. EFFECT OF MERCERIZATION ON COTTON TWILL

| NaOH (%) | Exposure time | Contrast ratio |
|---|---|---|
| None | as received | 1.25 |
| None | treated with water | 1.25 |
| 20 | 2 min. | 1.33 |
| 23 | 2 min. | 1.33 |
| 26 | 2 min. | 1.34 |
| 26 | 5 min. | 1.32 |
| 26 | 10 min. | 1.32 |
| 29 | 2 min. | 1.32 |

a disadvantage, for showing differences, in comparison with the results on fabrics.

*Mechanical Effects on Fabric Structure*

Several variations of drying conditions and low pressure mechanical smoothing are compared in Tables III and IV. The drying stage was varied in order to give an added effect on the luster produced by the resin application. All samples were dried to some extent at 5% stretch in each direction on a pin frame. Samples referred to in Tables III and IV as "dried-on" were completely dried in the oven before their removal from the pin frame. This procedure was intended to correspond to drying on a tenter frame in a finishing plant.

The samples designated "completely dried, ironed" in Table III were ironed with a hand iron set at 400°F after being completely dried, but before curing the resin. The samples designated "partly dried, ironed" in Table IV were dried to a semidry condition, removed from the pin frame, and ironed completely dry with a hand iron set at 400°F. The fabric in this instance was just moist, about the degree of dampness used for household ironing, before the ironing was begun. The samples designated "damp ironed" in Table IV were subjected to 30-sec. drying in the oven to eliminate the wrinkles and set the sample size before ironing, and were still distinctly wet at the start of ironing.

Less effect on luster is obtained by completing the drying on the tenter frame, designated "dried-on" in the tables, than in the other variations of low pressure mechanical smoothing. However, even in drying on the tenter, there is a straightening effect on both warp and filling yarns, which, being set when the resin is cured, could contribute to the increased luster.

In almost every trial, higher luster is obtained by ironing the partially dried fabric than by ironing either the completely dried fabric (Table III) or the damp fabric (Table IV). This is fortunate, since the calendering process, which would be used in continuous production instead of ironing, can be applied to partially dried material but would not be as practical on really wet material.

These experiments confirm the directions given by several resin suppliers [4, 5] which indicate that the moisture control is critical in the production of calendered, glazed, or embossed finish effects.

*Comparison with Mercerization*

Mercerization has been carried out on the same fabric, with the results shown in Table V. The fabric was stretched 5% in each direction during the mercerization and until the caustic was neutralized, the same degree of stretch as that used in the resin treatments. On this fabric, the resins when merely dried-

TABLE VI. LABORATORY EMBOSSING COMPARED WITH TENTERING AND IRONING

| Treatment | Pressure (p.s.i.) | Thickness at 0.1 lb./in.² Before washing (mils) | After 1 wash (mils) | After 10 washes (mils) | Luster (contrast ratio) 1 Wash | 10 Washes | Wrinkle recovery (%) | Stiffness (mg.×cm.) | Tensile strength (lbs.) |
|---|---|---|---|---|---|---|---|---|---|
| Original fabric | | 20 | | | 1.25 | | 46 | 209 | 91 |
| Tenter, dried-on | | | 21 | | 1.36 | | 72 | 217 | 71 |
| Partly dried, ironed | | | 20 | | 1.39 | | 72 | 278 | 69 |
| Partly dried, emboss | 500 | 15 | 20 | 19 | 1.50 | 1.38 | 73 | 270 | 67 |
| Metal-cloth-metal | 2,000 | 13 | 20 | 18 | 1.57 | 1.45 | 71 | | |
| | 8,000 | 10 | 17 | 17 | 1.87 | 1.56 | 69 | | |
| Damp, emboss | 500 | 12 | 18 | 18 | 1.81 | 1.47 | 66 | 350 | 62 |
| Metal-cloth-metal | 2,000 | 12 | 18 | 18 | 1.74 | 1.53 | 69 | | |
| | 8,000 | 9 | 16 | 17 | 2.23 | 1.52 | 61 | | |
| Damp, emboss | 500 | 14 | 19 | 18 | 1.66 | 1.48 | 73 | 330 | 60 |
| Metal-cloth-cloth | 2,000 | 12 | 17 | 18 | 2.03 | 1.52 | 71 | | |
| | 8,000 | 12 | 16 | 17 | 2.15 | 1.65 | 65 | | |

on produce the same increase of contrast ratio as mercerization. When mechanical smoothing is combined with resin treatment, the contrast ratio goes even higher than it does with mercerization. While there may be some differences of subjective impression of luster in the two cases, with more of an impression of flattening, film formation, or glazing for the resin-treated fabrics which have been ironed, there is a general similarity of impression of luster between these and the mercerized fabrics.

*Embossing*

Higher pressure mechanical smoothing, a laboratory version of embossing, was carried out with a laboratory-scale hydraulic press equipped with heated platens. Thin, smooth, polished sheets of chrome-plated, brass "ferrotype" plate used by photographers were cut to various size and placed between the press platens and the fabric.

Three sizes of metal plates were used, 6 × 6, 3 × 3, and 1.5 × 1.5 in., so that the total pressure of 18,000 lbs. was applied at 500, 2,000, and 8,000 lbs./sq. in.

A modified urea formaldehyde resin, UFMA, offered for embossed effects was used at 10% add-on. The fabric in the various degrees of dryness was placed in the press for 4 min. at 150°C. The backing of the fabric was changed in two ways in order to determine the best procedure for producing a high sheen. The samples designated as "metal-cloth-metal" (Table VI) had a polished sheet on both sides of the sample. The samples marked "metal-cloth-cloth" had metal on the face of the cloth and a fabric on the back of the sample.

After the embossing and curing, the thickness was measured, before the fabric was washed, in order to determine the greatest degree of flattening, with the results shown in Table VI. Thickness and contrast ratio were also measured after the first and tenth washes, and other fabric properties, where sample size permitted, after the first wash.

TABLE VII. Polymerization of Resin in or on the Fibers 60/2 Cotton Yarn, Resin Dried and Cured on Taut Skeins

| Resin | Luster (contrast ratio) Mercerized | Kiered | Theoretical location |
|---|---|---|---|
| MFC | 2.78 | 1.67 | in |
| MFC acid colloid | 2.50 | | on |
| None | 2.98 | 1.61 | |

Laboratory embossing carries the contrast ratio to higher values with increased pressure and increased flattening of the cloth structure. Even after 10 washes the order of rank in contrast ratio is the same as at first, with only one exception. The luster of the embossed areas has noticeably different characteristics from that of mercerized fabrics in that one sees definite flattening, but the effect does permit development of increased highlight and sheen.

The various conditions of embossing all lead to higher values of luster, as measured by contrast ratio, than the low pressure ironing. In the embossing series, greater shine is produced on moist than on partially dry fabrics. Under these conditions the moisture relations also appear to make more difference than the kind of backing. It should be noted that the conditions of these laboratory tests differ considerably from those of practical embossing, especially in that the fabric was held in the press long enough to dry it. However, these results indicate the importance of control of moisture in practical embossing, as has been pointed out by suppliers of resins [4, 5].

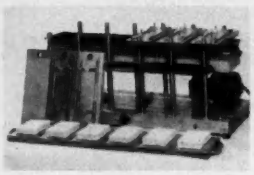
*Polymerization in or on the Fibers*

It has been noted that all of the resins examined on mercerized yarns decreased the luster, and that similar effects were seen in limited trials with rayon filament yarn and fabric. This indicates increased

TABLE VIII. Effects on Properties Other Than Luster

| Property | Untreated control | Range in different resins | Effects of mechanical treatments: Light calendering *versus* tentering | Embossing *versus* light calendering |
|---|---|---|---|---|
| Wrinkle recovery | 46% | 62%–89% | variable direction; differences 0%–8% | decreases; differences to 8% |
| Stiffness (flexural rigidity, mg. × cm.) | 209 | 180–470 | increases; differences 20–60 | increases; differences 70 or more |
| Tensile strength, warp ravelled strip, lbs. | 91 | 50–80 | variable direction; differences 2–5 lbs. | decreases; differences 9 lbs. or more |
| Tear strength, trapezoid, warp threads torn | 6 | 1–4 | decreases; difference 1 lb. | not measured |

# PILLING TESTER



- Ease of Comparison Data
- Simple
- Capacity 6 Test Specification
- Versatile
- Reproducibility of Results

The pilling tester was designed to furnish the technician with an instrument to check the problem of pilling. With this instrument, man made fibers in staple form, fugitive finishes, and other added materials affect the pilling propensities of new fabrics so that pilling before and after washing and/or dry cleaning frequently gives valuable information. This tester can be used as a control tester for fabrics in commercial production or as a research tool in the development of new fabric constructions or in studying variations in manufacturing processes.

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scattering of light, which might be the effect of resin particles on the surface of smooth fibers.

A larger effect is observed in a set of tests, in which a melamine formaldehyde resin is compared with its acid colloid, prepared by partial prepolymerization with acetic acid [6, 11]. The acid colloid, which should be less able to diffuse into the fibers and therefore should be more of a film on the fibers, does lower the luster of mercerized yarn further than its more diffusible precursor applied in the usual way, as shown in Table VII.

In further evidence that the resin produced from the acid colloid is on the fibers rather than within, the wrinkle recovery [2] of fabric to which this acid colloid preparation had been applied was only 36% to 40%, while the original cloth showed 46% recovery and the other resin treatments ranged above 60%.

The effect of the acid colloid on luster of fabric, however, was in the same range as the other treatments, as shown in Table IV. This indicates that it has effects on fabric structure similar to those of the other resins which, however, were deposited within the fibers to a much greater extent.

### *Effects of Resins on Other Fabric Properties*

Table VI shows effects of embossing procedures with one resin on certain fabric properties. These, and similar measurements on the treatments corresponding to tentering and light calendering in Table IV, have been summarized in Table VIII. The general level of each of the four properties examined is chiefly affected by the particular resin formulation, as far as variations between tentering and light calendering are concerned. It is probable that variation of formulation and of degree of polymerization at time of application will extend the range of the effects of individual resins, but that there are certain general levels for different types. However, variations of mechanical treatment also affect these properties, although wrinkle recovery [2] and tensile strength [3] seem less affected than stiffness [1] and tear strength [3].

These facts indicate that the finisher can properly choose thermosetting resins on the basis of stiffness and tear strength, or other properties which may concern him, such as tendency to stick to rollers in processing, and rely on mechanical processing and the durable control of fabric structure given by these resins for effects on luster.

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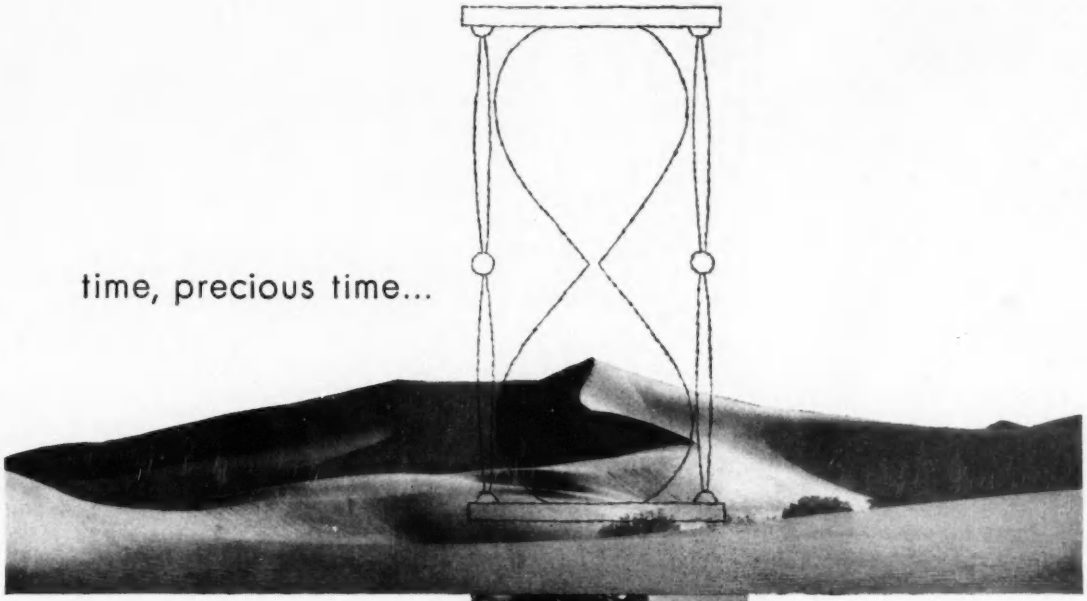

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